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Quantitative Produced Water Analysis using Mobile ^1H NMR

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Declaration

I, Lisabeth Wagner, certify that:

This thesis has been substantially accomplished during enrolment in the degree.

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Lisabeth Wagner
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Abstract

Accurate measurement of the oil concentration in discharge water is a key element of the oil and gas industry to demonstrate compliance with environmental regulations. This is becoming ever more important due to increasing produced water volumes across the globe and the development of subsea production facilities where the discharge of produced water directly at the wellhead is being considered. The most commonly deployed technologies for oil-in-water monitoring in the field are optical devices which infer the oil concentration through measurement of a characteristic property of the specific oil, for example its UV fluorescence intensity. These measurements are usually associated with the need to provide frequent (re-)calibration and their applicability is dependent on the specific hydrocarbon reservoir. A technology gap exists regarding accurate monitoring devices that operate reliably, independent of the hydrocarbon source and changing reservoir or production conditions.

In this context, the application of low-field Proton Nuclear Magnetic Resonance (^1H NMR) to quantitatively assess the oil concentration of aqueous samples is explored. Specifically, the feasibility of solid-phase extraction (SPE) for sample pre-concentration in a suitable solvent in combination with quantitative, low-field ^1H NMR analysis is presented as an alternative to the techniques currently deployed for oil-in-water monitoring. The aim of this thesis is thus to provide the proof of concept of a suitable SPE-NMR methodology and the subsequent development of this methodology into a working prototype to enable fully automated oil-in-water measurements.

The proof of concept, set up in a laboratory environment, showed that the application of SPE-NMR to samples of water contaminated with a light crude oil yields reliable results that compare favourably against the well-established methods of infrared absorbance and gas chromatography. Herein, the deployment of 1 % chloroform (CHCl_3) in tetrachloroethylene as the extraction solvent for the elution step in the SPE procedure presents the essential element as this renders the NMR analysis self-calibrated. The extension of this SPE-NMR methodology is demonstrated to enable the separate quantification of the aromatic and aliphatic fraction of the total oil content in a sample. A twofold measurement approach was developed that uses two solvent mixtures with two reference compounds, CHCl_3 and hexamethyldisiloxane, to retain the self-calibrated characteristic of the original method. This Advanced SPE-NMR methodology was successfully applied to water contaminated with aromatic and aliphatic hydrocarbons.

The SPE-NMR methodology was further developed into a working prototype that ultimately enables automated solid-phase extraction and in-line NMR measurement. Initially, a semi-automated version was built that implemented the SPE procedure but required a manual NMR measurement. This prototype was tested extensively both in the laboratory as well as during a field trial at an onshore gas plant for confirmation of its applicability to a variety of samples and its functionality under field conditions. The semi-automated prototype was consequently extended to include the NMR spectrometer in-line thereby providing fully automated SPE-NMR analysis of produced water samples. Laboratory testing of this automated prototype and validation against infrared and gas chromatography analysis demonstrated its potential for reliable and autonomous oil-in-water monitoring.

In contrast to other oil-in-water measurement techniques, the proposed SPE-NMR prototype is a non-optical, self-calibrated device and able to detect both dissolved and dispersed oil components. Its greatest potential is in the form of a by-line measurement device as a complement to a continuous on-line sensor to provide compliance measurements, indications of process changes and confirmation of the on-line readings. In order to commercialise the SPE-NMR approach, optimisation of the current prototype with respect to the components used and implemented flow path is recommended. Furthermore, the application to other water contaminants, such as organic acids, should be explored.

*Hinter den Bergen, den Städten, den Flüssen und Strömen,
den Fotos und dem letzten Geld
Mit deinen Narben, alten Platten, deiner Hoffnung, diesem T-Shirt
am anderen Ende der Welt*
- Thees Uhlmann

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Authorship Declaration: Co-Authored Publications

The thesis contains published and future publications, which have been co-authored. The details of the publications, the contributions of authors and the chapters they appear in thesis are set out as follows:

1. *Quantitative produced water analysis using mobile ^1H NMR* by L. Wagner, C. Kalli, E.O. Fridjonsson, E.F. May, P.L. Stanwix, B.F. Graham, M.R.J. Carrol and M.J. Johns; Measurement Science and Technology 2016, 27.

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Student contribution to work: Development of the measurement methodology, carried out all experimental work, data analysis and interpretation and uncertainty calculations. Primary contributor to manuscript preparation.

Student signature:

Date: Sunday 27th January, 2019

I, Michael Johns, certify that the student statements regarding their contribution to each of the works listed above are correct.

Coordinating supervisor signature

Date: Sunday 27th January, 2019

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Chapter 1

Introduction

The ultimate goal of this doctoral research is the development, construction and testing of a prototype for quantitative analysis of the oil content in produced water. This will be achieved by implementing solid-phase extraction in combination with benchtop, low-field Proton Nuclear Magnetic Resonance (^1H NMR). Produced water is trapped in underground formations together with hydrocarbon resources and brought to the surface during extraction processes. It is a complex mixture that can include formation water from the reservoir, water that had been injected for enhanced hydrocarbon recovery, production chemicals used in the process and condensed water from the cooling gas stream. Figure 1.1 shows a simplified schematic of a subsea oil and gas reservoir, where the hydrocarbon sources are trapped with formation water in a permeable rock formation.

The extraction of produced water along with the main product of oil, condensate and/or gas from the reservoir is unavoidable. In the oil and gas industry, produced water is the single largest waste stream, both onshore and offshore, and the volumes have continuously increased over recent years (refer to Figure 1.2). In the US, approximately 7 to 10 barrels of produced water are generated for every barrel of crude oil [3]. The US Department of Energy's Argonne National Laboratory estimates the annual volume of produced water in the United States to be 21 billion barrels, in addition to approximately 50 billion barrels assumed to be generated in the rest of the world [4]. Worldwide, the average ratio of water to oil produced is between 2:1 and 3:1 [5]. This ratio generally increases with the age of a hydrocarbon reservoir and is unique for each well.

The composition of the produced water itself is complex and varies for each well, the production process and the age of the reservoir. Generally, it contains some of the hydrocarbons from the source reservoir along with production chemicals as well as other constituents present in the reservoir. Of

Figure 1.1 Schematic of a subsea hydrocarbon reservoir where crude oil, natural gas and formation water are trapped under an impermeable cap rock.

Figure 1.2 Global produced water volumes from onshore and offshore oil production [2].

these, the components of environmental concern are [6]: salts; oil and grease (OG); BTEX (benzene, toluene, ethylbenzene and xylenes); polyaromatic hydrocarbons (PAHs); organic acids (this includes in particular naphthenic acids); phenols (specifically short-chain alkyl phenols which have detrimental biological effects to marine life); some of the natural inorganic and organic compounds; and the chemical additives that are used during the drilling and extraction processes. Consequently, management of the produced water remains one of the major challenges of the oil and gas industry, as direct discharge or re-usage cannot be done without prior treatment to lower the amount of contained contamination.

On offshore production platforms, produced water is most commonly discharged to sea. In this case, the relevant environmental legislation limits the permissible hydrocarbon content in the discharged water. Furthermore, continuous overboard discharge from offshore production platforms is only allowed if the operator, i.e. the individual, company, trust, or foundation responsible for the production of the specific reservoir, reports the contained oil contamination measured with an approved measuring device. Measurement of oil-in-water (OiW) is a complex task given that the term "oil" is not unambiguously defined. Furthermore, crude oil (or condensate) is a complex mixture of different compounds with its exact composition varying between different reservoirs and changing over the reservoir's life. The permitted concentration of hydrocarbons in the discharge water is limited to mg/L (ppm) levels; for example for oil and gas production platforms installed in the North Sea, the maximum value is set to 30 mg/L [7].

Accurate measurements of oil-in-water are required from an operational point of view in order to optimise the production and produced water treatment so that less oil is discharged, chemical injection is minimised, process capacity is increased, and oil and/or gas production is maximised.

Automated on-line or by-line measurements are preferred over manual sampling and laboratory analysis to limit the time spent on the task. Therefore, the industry wishes for a robust OiW sensor that provides reliable, automated measurements and requires minimal maintenance.

Aside from the well-established offshore production platforms and associated overboard discharge of produced water, subsea treatment and disposal of produced water directly at the wellhead is emerging as an important development. This is becoming ever more important as the industry moves towards unlocking hydrocarbon sources at greater water depth (refer to Figures 1.3 and 1.4).

Figure 1.3 Global offshore oil production (including lease condensate and hydrocarbon gas liquids) by water depth in million barrels per day [8].

Figure 1.4 Schematic of Shell's history of deepwater production [1].

Introduction

The possibility to separate and subsequently either discharge or re-inject the produced water at the seabed brings economical and operational benefits. For example, avoiding the need to transfer the extraction product as a two-phase or three-phase stream from the wellhead to the topside platform or even onshore for separation and treatment simplifies flow assurance (e.g. less risk of hydrate formation) and lowers production costs (reduced flowline size, less equipment on surface production platform). However, a few technology gaps persist impeding the implementation of subsea separation and treatment systems. One of these gaps is related to the requirement of reporting the discharge water quality in terms of oil-in-water content. The harsh subsea environment poses additional challenges to a reliable and accurate measurement and requires the sensor to perform autonomously for an extended period of time. To date, very few studies exist testing the ability of oil-in-water sensors for subsea deployment.

The growing awareness regarding both environmental pollution and operational detriments of the available OiW sensors drive the continuous development of new instruments for laboratory, onshore, offshore and subsea application. Most of the currently applied OiW monitors use ultraviolet (UV) fluorescence (on-line) or infrared (IR) absorbance (manual laboratory method). None of these options has the ability to intrinsically measure the total oil content; UV fluorescence measures the aromatic content and IR the aliphatic hydrocarbons that contribute to the total oil contamination. Thereby, the other fraction of the oil contamination — aliphatics for UV fluorescence and aromatics for IR — is derived by assuming a constant ratio of aromatics to aliphatics. Most of the currently available technologies for automated oil-in-water measurements are optically based. This includes image analysis, UV fluorescence and light scattering. For these sensors, fouling of the optical window resulting from the oil content or scale formation can have a detrimental effect on the ability to perform accurate measurements. Usually, an automated cleaning mechanism is included in the device to maintain operability. A gap still exists with regards to OiW monitors that determine the oil content accurately and reliably without the assumption of constant oil composition and further apply a non-optical measurement principle. In the context of subsea application, the need to frequently calibrate the sensor and ensure the cleanliness of the optical window can become a big cost and time factor. Either intervention by remotely operated vehicles (ROVs) or retrieval of the sensor is required to perform adequate maintenance.

¹H NMR spectroscopy can prove to be very useful with regards to conducting reliable quantitative measurements due to its non-optical nature and the capability to provide detailed information about the sample composition. Furthermore, accurate quantitative analysis is readily implemented by adding a reference compound to the sample of interest and thereby establishing an effectively self-calibrated measurement. Historically, quantitative NMR was performed with high-field spectrometers, such as the one shown in Figure 1.5a, due to their excellent spectral resolution and high sensitivity. These are limited to applications under laboratory conditions, are expensive and bulky. Within the past two decades, increasingly robust and more cost-effective low-field NMR spectrometers have been developed for application in more challenging environments. Examples are

the NMR Mouse [9], which was developed as a portable device to be applied in the fields of material science and biomedicine, or the Phyton-NMR [10] (a photo can be seen in Figure 1.5b) for the analysis of liquids in plants.

(a)

(b)

Figure 1.5 (a) High-field NMR spectrometer installed in a laboratory under controlled surrounding conditions. (b) Portable NMR device (Phyto-NMR) for the application of moisture content determination in fruits, stems or leaves [10].

Compared to optical spectroscopy methods, NMR has an intrinsically low sensitivity (the reasons for this will be discussed in Chapter 2). Therefore, in order to achieve a quantitative, self-calibrating measurement of the OiW content at low mg/L values, the oil contamination has to be extracted from the produced water and pre-concentrated in a suitable solvent. In the context of this doctoral research, solid-phase extraction (SPE) is the selected method for such sample preparation. SPE is readily automated, and the proposed approach of SPE in combination with low-field NMR can be a viable option for quantitative produced water analysis.

Following an introduction to the fundamental theory relevant for this doctoral research (Chapter 2), the proposed approach of using solid-phase extraction in combination with low-field ^1H NMR (referred to as SPE-NMR) for the quantification of light crude oil in produced water is detailed and tested to provide proof of its feasibility (Chapter 3). The SPE-NMR methodology is subsequently expanded to enable the individual assessment of the aromatic and aliphatic hydrocarbons that contribute to the total oil content in produced water (Chapter 4). Chapter 5 then describes the design, development and construction of a prototype that implements the SPE-NMR in an automated procedure. Finally, the developed prototype is tested with respect to robustness and repeatability (Chapter 6), both in the laboratory and during an onshore field trial. A comprehensive conclusion and potential future work are provided in Chapter 7.

Chapter 2

Fundamentals

This chapter provides the theoretical fundamentals relevant in the context of this doctoral research. In the first section, Section 2.1, produced water management and oil-in-water monitoring options currently applied in the industry are detailed. The theory of nuclear magnetic resonance is described in Section 2.2 providing the reader with the basics pertinent to this thesis; the reader is referred to one of the many textbooks available on NMR if a more profound understanding is desired [11, 12]. Lastly, sample preparation using solid-phase extraction is explained in Section 2.3 with specific focus on the application to produced water.

2.1 Produced Water Management and Monitoring

Several options for the management of produced water exist; this includes re-injection into the well for enhanced recovery, re-use for a different purpose or discharge to the environment. On offshore installations, environmental discharge is the most commonly used approach [6]. However, both for discharge or re-use, produced water is required to meet quality specifications depending on the intended purpose of the stream.

For environmental discharge, regulatory authorities define the hydrocarbon concentration limit in discharged produced water in terms of oil and grease (US EPA [13]) or dispersed oil (OSPAR — Convention for the Protection of the Marine Environment of the North-East Atlantic [14]). Prevalence of other constituents, especially the amount of total suspended solids (TSS), are of significance when the water is re-injected into the reservoir or intended to be re-used for a different purpose. A variety of methods, based on physical, chemical and biological approaches, have been developed to treat the produced water to meet environmental and quality requirements. Offshore, where space is limited, chemical — coagulation/flocculation through injection of chemicals, demulsification, etc. — or physical treatment — adsorption, filters, cyclones and others — prevail [15]. Here, the main objective is to reduce the oil content down to the required concentration to allow discharge. If the water is not

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discharged to the environment, it is re-injected into the reservoir for enhanced recovery. In this case, the water quality usually has to meet stricter and more specific requirements that also depend on the reservoir. Oil and solids content are particularly important since well plugging and/or reduced injectivity are to be avoided. Less than 42 mg/L for oil and 10 mg/L in regards to total suspended solids (TSS) are generally considered acceptable in this context [16]. Low salinity [17] and water softness [18] help ensure that the wettability does not change from water-wet to become oil-wet, which effectively inhibits oil recovery [19]. Treatment of produced water for re-injection is complex and more expensive than using seawater for enhanced recovery, thus discharge is still the most widely applied management method offshore [16]. Onshore facilities on the other hand can generally deploy more comprehensive treatment technologies as real estate is not an issue, and often combine different approaches in several treatment stages. Here, discharge to surface waters is the last option to be chosen only when the alternatives, such as re-injection or discharge to a disposal well, cannot be realised [20]. Legislative limits for discharge to surface waters are rather restrictive regarding contained contaminants. Not only the oil content but also salinity, chemical additives, naturally occurring radioactive materials and other inorganic and organic compounds are of concern [21]. Control of pollutant discharge to receiving surface water and/or groundwater is effected by means of strict effluent limits [22]. The preferred management method for onshore facilities is treatment and re-cycling, where the treatment requirements are specified by the secondary user. Options include crop irrigation, wildlife and livestock consumption, industrial processes, dust control, and more [22].

The conventional treatment of produced water usually deploys a primary two or three phase separation system, often an API separator (designed according to the standards published by the American Petroleum Institute), to separate the aqueous from the oil rich phase (refer to Figure 2.1 for a schematic representation).

Figure 2.1 (a) Schematic representation of the primary separation stage of an oil production process. (b) Example of an API Gravity Separator for separation of the three phases oil, gas and water.

Downstream of the primary separation stage, the oil rich stream is treated and purified in an oil treatment package whereas the water undergoes further treatment separately. Typically, the water is treated and polished in several steps including a primary treatment, such as hydrocyclones or corrugated plate separators. Subsequently, secondary treatment is applied, which most commonly

2.1 Produced Water Management and Monitoring

consists of gas flotation units. Table 2.1 shows a summary of the most used widely technologies for de-oiling produced water (primary and secondary stage), indicating their efficiency according to minimum size of removable particles [23]. Refer to Figure 2.2 for schematics showing the typical design of a corrugated plate separator, an induced gas flotation unit and a hydrocyclone.

Table 2.1 Oil content removal technologies according to the minimum size of removable particles [23].

Oil removal technology	Min size of particles removed [μm]
API gravity separator	150
Corrugated plate separator	40
Induced gas flotation (without / with flocculants)	25 / 3 - 5
Hydrocyclone	10 - 15
Mesh coalescer	5
Media filter	5
Centrifuge	2
Membrane filter	0.01

Figure 2.2 Schematic showing the typical design of a (a) Corrugated Plate Separator, (b) Induced Gas Flotation Unit and (c) Hydrocyclone for separation of oil from produced water.

In most cases, however, these conventional treatment technologies are not able to meet the quality requirements for discharge or secondary usage of produced water and further polishing treatment has to be deployed [24]. In 1995, the American Petroleum Institute published recommendations regarding Best Available Technology (BAT) for the treatment of offshore effluents — these include physical adsorption, air stripping, membrane filtration, ultra-violet light irradiation, chemical oxidation and biological treatment [25]. Since that time, treatment technologies have been further developed, enhanced and renewed. Industry operators are facing the challenge of evaluating the available technologies, the current legislative requirements and then have to choose the most cost

effective approach according to the specific produced water stream, its constituents and volume as well as the intended purpose after treatment.

2.1.1 Offshore Produced Water Discharge Regulations

The dominant produced water management method on offshore platforms is direct discharge to the environment. The operator has to comply with environmental legislation that limits the permissible hydrocarbon content in the discharge stream. National and/or regional authorities are responsible for issuing discharge permits and defining relevant reference methods to measure and report the hydrocarbon content. The limits in the different jurisdictions for offshore discharge vary globally between 10 mg/L (Tunisia) and 100 mg/L (Thailand and Malaysia) [26].

In the United States, according to the requirements set by the Environmental Protection Agency (EPA), the monthly average of oil and grease in the produced water discharge stream is 29 mg/L and the daily maximum at 42 mg/L [27]. The OSPAR Convention has set the goal for "zero harmful discharge" by 2020 [28, 29]. However, the current limit for any offshore installation in the regulatory region of the OSPAR is 30 mg/L of dispersed oil as detailed in the OSPAR Recommendation 2001/1 [14]. In Australia, previous legislation setting a limit of 30 mg/L of petroleum in produced water discharged into the sea was repealed and replaced. The new amendment to the regulation, enacted in 2014, requires the reduction of environmental impacts and risks to be as low as reasonably practicable (ALARP) [30]. Nevertheless, the 30 mg/L limit is still relevant alongside the requirement to demonstrate that the best available technique is chosen in terms of produced water treatment.

2.1.2 Oil-in-water Monitoring

Oil in produced water is not an unambiguously defined term. In general, dispersed oil and dissolved oil are distinguished. Dispersed oil means the oil contained in form of droplets, whereas dissolved oil are the components that are dissolved in the aqueous phase. The oil content in produced water is a method-dependent parameter as both sample preparation and the actual measurement method have an impact on the obtained value. Because of the complexity of the oil composition and the presence of other contaminants in produced water, quantitative analysis usually involves the measurement of a characteristic property of the oil to subsequently infer the oil-in-water concentration. No measurement exists that is able to directly measure the total oil content of a produced water sample.

In order to compare data from different installations, regulatory bodies define the relevant reference method. Reference methods are also used to drive future legislation, for compliance monitoring and certification of measurement methods for their application in the field. Currently, three different types of reference methods are available: gravimetric, infrared absorption (IR) and gas chromatography with flame ionisation detector (GC-FID). The IR based method involves acidification

2.1 Produced Water Management and Monitoring

of the produced water sample followed by extraction of the oil content using a suitable solvent. After drying and purifying, the extract is measured in an IR spectrometer. The oil content of the original sample is calculated by comparing the absorbance of the extract to that of a sample with known oil concentration. Infrared spectrometers apply a single wavelength, generally around 2930 cm^{-1} , or triple wavelength, at 3030 cm^{-1} , 2960 cm^{-1} and 2930 cm^{-1} , approach [31]. Historically, halogenated organic solvents, such as carbon tetrachloride or Freon, have been used as extraction solvents for IR measurements. However, due to environmental and health concerns, these solvents have been phased out while attempting to replace them suitable alternatives. Currently, the IR method according to ASTM D 7066 [32] is well-established on offshore and onshore installations using S-316 (mixture of dimer and trimer of chlorotrifluoroethylene) as the extraction solvent. Despite being non-toxic, S-316 is a very costly solvent and elaborate recovery techniques are implemented.

In the United States, the definition of oil and grease content is based on the extraction of the hydrocarbon content from the aqueous phase using n-hexane as the solvent. The exact procedure is detailed as "US EPA 1664A" [33]. This methods accounts for all organic material that can be extracted from water with n-hexane, is not absorbed on silica gel and does not evaporate during the drying process. US EPA 1664A is the most commonly applied of the available gravimetric methods.

In contrast to infrared and gravimetric, GC-FID methods yield more details about the hydrocarbon components present in the produced water. As with the methods described earlier, GC-FID measurements involve acidification of the sample and extraction using a suitable solvent. After drying and purifying, the extract is then injected onto a chromatographic column. The oil components are separated according to their retention time and then combusted and detected in the flame ionisation detector. The sum of the responses are compared to standards of known concentrations and the oil-in-water concentration can be calculated. For the North-Atlantic region, GC-FID is the relevant reference method, the exact procedure has been defined by the OSPAR Convention [34].

While being essential for comparison purposes and development of future legislation, reference methods are generally time- and labour-intensive and impractical for application in the field, especially offshore. Therefore, a variety of measuring tools have been developed for the analysis of oil-in-water in the field. These methods can be subdivided into on-line sensors and benchtop instruments. The latter are usually set up in a laboratory, correlated to the relevant reference method and are needed for compliance monitoring. Sampling from the produced water stream is still required, but the measurement is performed on site and as quickly as possible. On-line sensors on the other hand analyse the produced water stream either in-line or in a bypass line enabling process trending and optimisation.

Approved benchtop instruments are commercially available and well-established especially for offshore applications where quick results are desirable. In this context, infrared absorbance and ultraviolet (UV) fluorescence are the most commonly implemented techniques [35]. Various types of IR based analysers have been developed using different solvents and sample preparation methods.

The Horiba instrument (OCMA-500 Oil Content Analyzer), using S-316 solvent and near infrared absorption, is widely used on offshore platforms as well as for onshore oil-in-water analysis [31]. Another well-established and certified infrared instrument is the Eracheck (or Eracheck Pro) developed by eralytics GmbH. The Eracheck is also a chlorofluorocarbon (CFC) free method and uses a quantum cascade laser for the measurement, reporting the result as TPH or Total Oil and Grease (TOG) in water. Alongside IR instruments, UV fluorescence methods are the most commonly accepted options [31]. The underlying principle is the ability of some oil components, the aromatic hydrocarbons, to absorb UV light and then emit fluorescence light at a different wavelength. No CFC solvents are required for the measurement and the instruments are very sensitive. A variety of portable UV oil-in-water analysers are available on the market, such as the *TD550* from Turner Designs Hydrocarbon Instruments [36] or the *FluoroCheck II PPM Oil in Water Monitor* Arjay Engineering [37]. Besides infrared and UV fluorescence, benchtop colorimetric and imaging analysers are applied in field laboratories to measure ppm concentrations of oil in produced water, but are not as commonly applied as IR or UV fluorescence methods.

For the continuous, on-line measurement of oil-in-water, the most commonly applied methods are laser induced fluorescence (LIF), image analysis and light scattering [38]. LIF probes emit UV laser light into the produced water stream by fibre optics, the oil components interact with the light, re-emit fluorescence that is then detected and transmitted with the fibre optics. Light scattering techniques pass visible light through the produced water stream, where a portion of that light will be scattered due to the presence of particles, oil droplets and gas bubbles. Detecting the reduced amount of transmitted light as well as the angles of the scattered light yields the amount of oil contamination in the water stream. Image analysers work with high resolution video microscopes that capture images of the produced water stream in sequence at high speed and automatically analyse for visible solid particles, oil droplets and gas bubbles. The concentration of the oil contamination is calculated based on the field of view and determined volume of the particles.

When considering the well-established (mentioned above) and other less known methods, like photoacoustic or colorimetric, each has its advantages and disadvantages. One characteristic inherent to all presented approaches except imaging is the requirement for calibration of the instrument. In general, the oil content is indirectly measured, hence a correlation needs to be established between a property of the oil, for example the UV fluorescence or IR absorbance, and the oil concentration in the water. This implies that a calibration has to be established prior to measurement, preferably with the oil or condensate in question. In the case of a change in oil composition, calibration has to be repeated to maintain the reliability of the results obtained. Most commonly, the guidelines regarding the implementation of an on-line measurement require the correlation between the on-line sensor and an approved laboratory method [39] if the on-line measurement is to be used for reporting. This correlation has to be checked periodically; for example in the UK, a weekly test has to be carried out [39]. All commercially available on-line oil-in-water sensors are based on optical measurement principles. Optical windows are prone to fouling due to the contact with the contaminated water

2.1 Produced Water Management and Monitoring

stream, hence automatic cleaning mechanisms have to be implemented in order to retain functionality of the sensors [40]. This increases the complexity of the instrument and the risk of a malfunction of the sensor. However, manufacturers are constantly improving their technologies making the components more robust, minimizing size and providing fully automated measuring devices for on-line application.

Apart from the established onshore and offshore oil and gas extraction facilities, efforts are moving towards subsea separation and processing to optimize production costs and efficiency [41, 42]. Unlocking remote hydrocarbon sources in deep water locations is increasingly attractive [43], but relies on available technologies that are compact and robust for reliable production on the seabed. In this context, new challenges arise for produced water treatment as industry wishes to dispose of the produced water directly at the well-head to avoid its transfer to the surface or shore for separation and treatment. This requires subsea separation of oil and water as well as a subsea treatment system to meet the discharge limits. Thus, reliable oil-in-water analysers need to be installed subsea to provide continuous contamination measurements. To date, no oil-in-water sensor has been certified for application subsea [44, 45], but a number of initiatives have been launched globally to address the issue. One example is the RPSEA project (2014 — 2016) "2012 Ultra-Deepwater Subsea Produced Water Sensor Development". As part of this project, three existing commercial oil-in-water analysers were tested and evaluated in respect to subsea application and a new sensor for subsea oil-in-water measuring was developed [46]. The commercially available oil-in-water sensors investigated apply microscopic imaging (JM Cauty, Inc.), light scattering (Digitrol) and UV fluorescence (ProAnalysis). The sensor designed and developed as part of this project deploys a new approach for oil-in-water metering, Confocal Laser Fluorescence Microscopy (CFLM). CFLM essentially combines UV fluorescence with high resolution microscopy, where UV fluorescence is used to distinguish oil droplets and oil coated solids from solid particles and gas bubbles. Image analysis is used for the calculation of concentration and size distributions and further enables the extension of the measurement range up to 10 % oil content. The CFLM sensor *OilWatcher* is now commercially available from ClearView Sensing [47]. The project showed the potential of the four sensors for subsea application and established the respective technology readiness level (the sensor from Digitrol is already available for subsea installation). Further efforts are driven by ExxonMobil [48] with the development and testing of microscopic imaging sensors to meet subsea requirements. Equinor (formerly Statoil) recently performed a surface trial with three techniques — microscopy, LIF and ultrasonic acoustic — and will progress to select one of them for marinization [45]. As the oil and gas industry comes closer to being able to perform subsea separation of oil and water, the necessity for a verified, reliable subsea oil-in-water sensor is becoming more urgent.

In the context of achieving reliable, robust and automated measurements of the oil content in produced water, low-field Proton Nuclear Magnetic Resonance (^1H NMR) has some unique features and high potential for application. NMR spectrometer are non-optical devices and have the ability to perform self-calibrating measurements. As opposed to the methods that are established in the oil and

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gas industry for produced water monitoring such as IR or UV fluorescence, the measurement with ^1H NMR can technically capture every compound that has hydrogen atoms in its structure and thus does not rely on a constant contaminant composition. This doctoral research proposes low-field ^1H NMR analysis in combination with solid-phase extraction (referred to as SPE-NMR) for sample preparation as a complement to the currently available oil-in-water monitoring devices. Table 2.2 summarises the commercially available technologies as well as the proposed SPE-NMR approach for oil-in-water measurements.

Table 2.2 Abilities and limitations of commercially available and potential technologies for oil-in-water sensors.

Technology	Application	Capabilities	Limitations
SPE-NMR	By-line & laboratory	Aromatic & aliphatic hydrocarbons, self-calibrated, non-optical	SPE required, no continuous measurement
UV fluorescence	On-line & laboratory	Quick measurement, no sample extraction needed, well established	Only aromatic content measured (dissolved), requires calibration, optical, interferences from production chemicals
IR absorbance	Laboratory	Industry standard	Aliphatics only, sample extraction & calibration required, expensive or toxic solvents
Ultrasonic acoustics	On-line & laboratory	Quick measurement, no sample extraction, not optical	Dispersed oil only, calibration required
Microscopy	On-line	Droplet sizing, solids content & particle sizing	Dispersed oil only, interferences from other components
CFLM	On-line	Droplet sizing, solids content & particle sizing	Calibration required, optical, dispersed & fluorescing oil components only
Light scattering	In-line, by-line, laboratory	Well established,	Dispersed oil, calibration required, optical window, interferences from solids & gas bubbles

2.2 Proton Nuclear Magnetic Resonance

This section provides an introduction into the basic principles of nuclear magnetic resonance (NMR) and, with relevance to the doctoral research presented here, a more detailed description of low-field spectrometers and quantitative NMR. For more in-depth explanations of the theory of NMR, the reader is referred to one of the excellent textbooks available on the topic [11, 12, 49, 50].

Nuclear magnetic resonance was first detected in early 1938 in nuclear beam experiments by Rabi [51], but it took another eight years [52] until a measurable signal was obtained from solid and liquid bulk material by Purcell [53] and Bloch [54], respectively. The relevance to chemical research was discovered as early as the 1950's, and later, in 1971, Lauterbur [55] first reported on the possibility to generate 3D images with NMR, a technique now called magnetic resonance imaging (MRI). Since then, NMR and MRI have become indispensable in the field of medical, chemical and physical research and MRI is one of the standard clinical diagnosis tools. Industrial applications of NMR have seen continuous development within the past 40 years [56, 57]. With more recent advancements in magnet design of the low-resolution or low-field spectrometers, NMR was able to break new ground in the fields of quality control and quality assurance [56]. Low-field spectrometers are better suited for industrial environments due to being smaller, mobile and more robust and are now well established in the industry [58–60].

2.2.1 Principles of NMR

Nuclear magnetic resonance originates from nuclear spin, which is another form of angular momentum and an intrinsic property of the atomic nucleus. Similar to the classical angular momentum arising from the rotation of an object, the nuclear spin angular momentum is a vector quantity that has a magnitude and direction. However, the nuclear spin does not arise from a spinning or rotational movement. The magnitude of the spin angular momentum is given by $J = [I(I+1)]^{-1/2} \hbar$ [50] with the spin quantum number I taking on integer values $I = 0, 1, 2, \dots$ or half-integer values $I = 1/2, 3/2, 5/2, \dots$ and $\hbar$ is Planck's constant divided by 2π . Associated with the nuclear spin is a magnetic (dipole) moment according to

$$\mu = \gamma J \quad (2.1)$$

γ is the gyromagnetic ratio, a constant for each nuclear isotope. NMR is concerned with manipulating and observing these quantized magnetic moments of nuclei. Of the nuclei with non-zero spin and natural abundance, hydrogen nuclei (protons, ^1H) have the largest γ -value with $\gamma = 2.675 \times 10^8 \text{ rad s}^{-1} \text{ T}^{-1}$ and therefore are the most commonly used nuclei for NMR. Exclusively protons are relevant to this thesis work, therefore the theory detailed in the following focuses on the NMR properties of these only.

When the nuclear spin vector is projected onto the z-axis, it takes on $(2I + 1)$ discrete values for the magnetic quantum number m with $m = -I, -I + 1, \dots, +I - 1, +I$. For protons with $I = 1/2$, this results in two possible values for m : $m = -1/2$ and $m = +1/2$. In the absence of a magnetic field, the distribution of the nuclear spins is isotropic. This condition is degenerate, all spin states have the same energy. When placed in an external magnetic field of magnitude B_0 , the nuclear spin state becomes $(2I + 1)$ -fold degenerate, meaning that the $(2I + 1)$ possible spin states are split and have slightly different energy levels. This interaction of the spins with a magnetic field is called the *Zeeman effect* and the energy separation accordingly *nuclear Zeeman splitting*. However, this does not mean that the spins have to be in one of the spin states, they generally are in a superposition or mixed state. The measurement of the proton nuclear spin in a magnetic field though will always give a result that shows the spins in either of the two possible states. Hence for a simpler approach, it is sufficient to assume that a nuclear spin is always in one of the defined spin states. The energy of a nuclear spin state can be calculated with:

$$E_m = -m \hbar \gamma B_0 \quad (2.2)$$

Transitions are only allowed when m changes by $+1$ or -1 . In the case of protons, where the gyromagnetic ratio is positive, the spin state with $m = +1/2$ is lower in energy and is given the label α or known as "spin-up" (the spin state $m = -1/2$ is referred to as the β state, "spin-down") [12]. This infers that alignment of the spin, and therefore the magnetic moment parallel to the direction of the external magnetic field, is preferential for a proton. Referring to Equation 2.1, a positive gyromagnetic ratio means that the direction of the magnetic moment has the same orientation as the spin. The energy that is required to transition from α to β can be provided by electromagnetic radiation as follows:

$$\Delta E = \hbar \gamma B_0 \quad (2.3)$$

The frequency of the allowed transition for a nuclear spin is known as the *Larmor frequency* ω_0 and defined as

$$\omega_0 = \gamma B_0 \quad (2.4)$$

For example, a proton in a magnetic field of 4.7 T has a Larmor frequency of 200 MHz, meaning that electromagnetic radiation with a frequency of 200 MHz (a radio frequency wave) will initiate transitions between the two energy states. When the r.f. source is turned off, the spins emit energy and return to their equilibrium state. The emission of this energy gives an oscillating voltage. For a single, uncoupled proton spin, a line at the Larmor frequency (here 200 MHz) would appear in a frequency domain spectrum.

The above description of nuclear magnetisation is based on quantum mechanics. A somewhat more comprehensible approach can be taken using classical mechanics and will be deployed in the following. When a spin-1/2 nucleus is placed in a magnetic field with magnitude B_0 , its magnetic

moment will start to move in a circular motion around the direction of the static magnetic field. The motion occurs on a cone at constant angle to the applied field and is known as *precession*. Precession is the result of the nucleus possessing nuclear spin and the magnetic moment experiencing a torque exerted by the magnetic field. A schematic representation of the precessional motion can be seen in Figure 2.3 where the nucleus is simplified as a sphere and the nuclear spin is shown as an arrow.

Figure 2.3 Precession of a nuclear spin at a constant angle θ in the presence of a static magnetic field of strength B_0 . The precession frequency ω_0 is the Larmor frequency defined by B_0 and the gyromagnetic ratio (Equation 2.4).

When a magnetic field is applied to a collection of protons, all of the spins will start to precess about the z-axis (direction of the static magnetic field) at the Larmor frequency with initially random orientations. As explained above, when a magnetic field is present, the degeneracy is lost and two possible energy states exist. The distribution between the high and low energy states can be determined with thermodynamics. When thermal equilibrium is established, the population of the energy levels, or the distribution of the magnetic moments α (up) and β (down), are determined by the Boltzmann distribution [49]:

$$\frac{N_{-1/2}}{N_{+1/2}} = \exp \left\{ \frac{-\hbar \gamma B_0}{k_B T} \right\} \quad (2.5)$$

Herein, $N_{-1/2}$ and $N_{+1/2}$ are the populations of the spins in the upper and lower energy states, respectively, k_B is the Boltzmann constant and T is the absolute temperature (K). Note that generally, magnetic moments have a preference to align themselves parallel with a magnetic field, such as a compass needle aligns itself with the direction of the earth magnetic field. However, the energy of the thermal motion is much greater than the interaction energy between the external magnetic field and the magnetic moments. At room temperature with a magnetic field of 5 T, the ratio between the upper and lower energy state populations is 0.999952, meaning that for 100000 spins in the lower state, there will be 99995 spins in the upper state. Thus the majority of the spins and their magnetic moment cancel out, but the slight excess of spins in the lower energy state gives rise to a net magnetic moment $\mathbf{M}$, a vector quantity with magnitude M and directed along the z-axis. This net magnetic moment is effectively what is measured in NMR experiments and because it originates from a very

small population difference, the inherent sensitivity of NMR is rather low. According to Equation 2.5, the signal-to-noise ratio can be enhanced by (i) increasing the sample volume, (ii) lowering the temperature or (iii) increasing the magnet strength. A homogeneous magnetic field across the sample volume is required so that all nuclei experience the same magnetic field. This limits the size of the sample volume and effectively impedes sufficient enlargement to boost the signal. Varying the temperature to manipulate the spin distribution was used frequently in the past when the resolution of NMR spectrometers was comparatively poor. However, depending on the sample concentration, the required cooling can be extreme and potentially has an adverse effect on the sample under investigation. Therefore, only option (iii) is feasible and the reason for the application of high field spectrometers for structure elucidation and compound identification where high sensitivity and resolution are essential.

The build-up of a net magnetic moment when exposed to a static magnetic field directed along the z-axis follows an exponential law [50]:

$$M_z(t) = M_z^0 \left(1 - \exp \left(-\frac{t - t_{on}}{T_1} \right) \right) \quad (2.6)$$

where M_z is the z-component of the bulk magnetisation vector, M_0 is the magnitude of $\mathbf{M}$ at thermal equilibrium and t_{on} is the moment when the external magnetic field is turned on. The time constant for the build-up of longitudinal magnetisation is T_1 , also known as the spin-lattice or longitudinal relaxation time constant. When aligned along the z-axis, the longitudinal- or z-magnetisation is almost not detectable, but it can be detected in the xy-plane perpendicular to the direction of the static field.

In equilibrium with the static field along the z-axis, the projection of $\mathbf{M}$ onto the xy-plane does not yield any x- or y-contribution, there is no magnetisation in the transverse plane as the spins are distributed symmetrically around the z-axis. However, through the application of a radio frequency (r.f.) pulse with a well-defined frequency, the longitudinal magnetisation can be excited away from the z-axis to give a measurable magnetisation in the transverse plane. The frequency required is determined by the Larmor frequency of the spins, the condition in which the frequency of the r.f. pulse matches the Larmor frequency is called resonance. The r.f. coil to produce an oscillating magnetic field is usually placed on the x-axis and tuned to match the Larmor frequency of the protons in the respective static field. Different tilt angles of the bulk magnetisation with respect to the z-axis can be achieved through variation of the length of the applied r.f. pulse. A pulse that causes an angular displacement of 90° , hence tilts the z-magnetisation entirely into the transverse plane, is called a 90° or $\pi/2$ pulse. Analogously, a pulse that inverts the z-magnetisation to point along -z is known as a 180° or π pulse. When the resonance condition is not met with the r.f. pulse, a residual z-magnetisation will persist and the resulting transverse magnetisation will be reduced.

2.2.2 Relaxation Mechanisms

After a r.f. pulse has been applied and the z-magnetisation or parts thereof is flipped into the transverse plane, the magnetisation will relax back to its thermal equilibrium along the z-axis. The relaxation process is described by two time constants T_1 (see also Equation 2.6) and T_2 . The longitudinal relaxation time constant (T_1) involves the release of the energy that the spins have gained through the applied r.f. pulse to the surroundings as the spins re-align with the static field along the z-axis. Essentially, this is the result of fluctuating magnetic fields that oscillate near the Larmor frequency and thereby stimulate the spins to emit energy and return to their equilibrium state. The rate of change of the bulk z-magnetisation can be described as follows:

$$\frac{dM_z(t)}{dt} = \frac{M_z(t) - M_z^0}{T_1} \quad (2.7)$$

Herein, the z-magnetisation $M_z(t)$ changes over time and reaches its maximum value M_z^0 along z when thermal equilibrium is re-established. T_1 depends on the substance under investigation, more specifically its phase, with most solids showing larger values for T_1 than liquids. This can be explained with facilitated thermal motion (Brownian motion) in liquids whereas the rigidity of solids restricts the thermal motion [61] - this effect is even more pronounced in crystalline structures (e.g gemstone diamonds have a ^1H T_1 in the order of days [62]). Typical longitudinal relaxation times for liquids are in the order of seconds (≈ 0.1 to 10 seconds). To determine T_1 for a given substance, either *inversion recovery* or *saturation recovery* experiments can be deployed. The inversion recovery pulse sequence consists of a π r.f. pulse to invert the z-magnetisation to point along -z, followed by a variable time delay and a $\pi/2$ r.f. pulse to measure the magnitude of $\mathbf{M}$ (the pulse sequence is shown in 2.4a).

Figure 2.4 Inversion recovery pulse sequence (a) where τ is varied and the resulting z-magnetisation plotted versus the time delay (b). The experimental data (dots) is fitted using Equation to yield the value for T_1 - the fit is shown as a continuous line.

By using Equation 2.7 and the initial state of $M_z(0)$ before the $\pi/2$ pulse is applied, the evolution of M_z with time is described through:

$$\begin{aligned} M_z(\tau) &= [M_z(0) - M_z^0] \exp\{-\tau/T_1\} + M_z^0 \\ M_z(0) &= -M_z^0 \\ M_z(\tau) &= M_z^0 (1 - 2 \exp\{-\tau/T_1\}) \end{aligned} \quad (2.8)$$

Herein, τ is the time after the π pulse at which the $\pi/2$ pulse is applied to flip the magnetisation vector into the transverse plane for measurement. The pulse sequence is repeated for different times τ and the intensity of the obtained signal plotted versus the time delay τ . Figure 2.4b shows the data of an inversion recovery experiment and the resulting fit.

Knowledge of T_1 is essential to determine the rate at which an NMR measurement can be repeated as full relaxation to equilibrium is required to avoid signal loss. For example, when applying signal-averaging to increase the signal-to-noise (SNR) in a pulse-and-collect measurement, the longitudinal magnetisation has to be effectively fully restored before subsequent excitation to ensure that maximum signal is obtained in the transverse plane. Typically, a repetition time (T_R) of 3 - 4 times T_1 is deployed to prevent significant partial saturation of the spins (saturation = equal populations in the energy levels resulting in no signal) and interference from residual xy-magnetisation [63]. A drawback of the inversion recovery method is the time delay between subsequent scans - at least $5 \times T_1$ - which leads to a long total experimental time. For a quicker T_1 estimate, the time τ at which no signal is recorded in the transverse plane can be identified by running a couple of experiments bracketing this "null point". Substituting $M_z(\tau) = 0$ and $\tau = \tau_{null}$ in Equation 2.8 gives:

$$T_1 = \frac{\tau_{null}}{\ln(2)} \quad (2.9)$$

Alternatively, the saturation recovery experiment can be used. This applies an initial $\pi/2$ pulse to saturate the spins and flip the magnetisation into the the transverse plane. Thereafter, a sequence of $\pi/2$ pulses with varying T_R are applied and the signal recorded in the transverse plane. If T_R is at least $5 \times T_1$, M_z will have returned to 99.3% of its equilibrium value along the z-axis [64] before the r.f. pulse and hence maximum signal intensity is achieved in the xy-plane. As full relaxation between subsequent scans is not required for the saturation recovery sequence, the overall experimental time is reduced compared to the inversion recovery experiment.

As opposed to T_1 , which describes the relaxation of the z-component of the magnetisation, T_2 or spin-spin relaxation characterises the evolution of transverse magnetisation. T_2 relaxation has an irreversible or non-secular and a (somewhat) reversible or secular contribution. The former is linked to the process of T_2 relaxation where small fluctuating magnetic fields, that are caused by adjacent protons, are responsible for both the return to thermal equilibrium along the z-axis as well as the decay of transverse magnetisation. The reversible contribution is the de-phasing of the spins or loss of

coherence as a result of inhomogeneities from the main magnetic field as well as susceptibility effects, chemical shift and, if applicable, magnetic field gradients. When the r.f. pulse is turned off, the spins resume their precession about the static magnetic field. Due to imperfections in the magnetic field homogeneity across the sample, each spin will precess at a slightly different frequency. As a consequence, the initial coherence of the spins is lost as all spins acquire different phases and the net magnetisation in the transverse plane diminishes. This loss of spin coherence can be reversed through application of a π pulse that effectively causes the spins to flip over in the transverse plane. Note that irreversible part of the spin-spin relaxation is a property of the sample, whereas the reversible part is inherent to the measurement/magnet.

When conducting a pulse-and-collect measurement and acquiring the voltage signal in the transverse plane, both relaxation mechanisms contribute to the signal decay and are measured. Labelling the irreversible contribution with T_2 and the reversible, secular part with T_2' , the combined relaxation constant T_2^* is given by:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2'} \quad (2.10)$$

When the assumption holds that the magnetic field is homogeneous across the sample and no susceptibility effects occur, $T_2^* \sim T_2$ and T_2 can be derived from the decaying signal in the transverse plane during a pulse-and-collect experiment. Alternatively, spin-echo pulse sequences are applied to determine the transverse relaxation constants of a specific spin system. The Carr-Purcell-Meiboom-Gill (CPMG) [65, 66] pulse sequence can be deployed to determine T_2 , the irreversible contribution to T_2^* . Here, an initial $\pi/2$ pulse, to bring the magnetisation into the transverse plane, is followed by a number of π pulses with different time delays in between. Through the application of the π pulses, the spin dephasing due to magnetic field inhomogeneities is refocused. The signal echo after each refocusing pulse is recorded showing an amplitude that decreases as the time delay between the pulses is increased. The observed signal decay is effected by the spin-spin relaxation alone. Analogously to the relaxation of the z-component of the bulk magnetisation vector (see Equation 2.8), the evolution and decay of the x- and y-magnetisation under the influence of T_2 relaxation can then be described as follows:

$$\begin{aligned} \frac{dM_{x,y}}{dt} &= -\frac{M_{x,y}}{T_2} \\ M_{x,y} &= M_{x,y}(0) \exp\{-\tau/T_2\} \end{aligned} \quad (2.11)$$

From the CPMG echo train, T_2 is derived from the decreasing signal amplitude of the echoes, whereas the individual decaying signals can be evaluated to give T_2' , the time constant of the spins dephasing as a result of magnetic field inhomogeneities.

2.2.3 NMR Signal Excitation and Detection

As mentioned above, to probe nuclear magnetisation, the spins have to be excited with electromagnetic radiation to transition between the energy levels. In the classical mechanic approach, this corresponds to tilting the z-magnetisation, which is established when a sample of nuclear spins is exposed to a static magnetic field pointing along the z-axis, away from the z-axis. This excitation in the presence of a strong static magnetic field is only effective when on resonance, hence it must be a magnetic field oscillating at or close to the Larmor frequency of the spins and typically is placed perpendicular to the main field. This field is called the B_1 field and is orders of magnitude smaller than the main magnetic field, but nevertheless able to effectively suppress the strong main field through resonance. Tuning of the r.f. coil to resonate at the correct frequency is essential to make sure that the resonance condition is met. The r.f. coil itself is part of the r.f. oscillator of the NMR spectrometer and is usually used both as the transmitter to turn the B_1 field on and off and the receiver to record the NMR signal.

The duration t and strength of the r.f. pulse B_1 determine the tilt angle β of the z-magnetisation ($\beta = \gamma B_1 t$). The amount of magnetisation aligned along z is hereby reduced to $M_z = M_z^0 \cos(\beta)$ whereas the transverse magnetisation is increased to $M_{xy} = M_z^0 \sin(\beta)$ as shown schematically in Figure 2.5a.

Figure 2.5 Result of a r.f. pulse around the x-axis. (a) Tip angle $\beta = \gamma B_1 t$ and the projection of the magnetisation vector with magnitude M_0 onto the -y-axis. (b) Rotation of the magnetisation vector with magnitude M_0 in the transverse plane at Larmor frequency ω_0 under the assumption that the tip angle was 90° .

When the pulse is switched off, the spins begin precessing about the z-axis again, which in turn initiates the precession of the bulk magnetisation vector. The rotation in the transverse plane of the x- and y-component of the magnetisation vector follows [50]:

$$M_x = M_{xy}(0) \sin(\omega_0 t) \exp\{-\tau/T_2^*\} \quad (2.12a)$$

$$M_y = -M_{xy}(0) \cos(\omega_0 t) \exp\{-\tau/T_2^*\} \quad (2.12b)$$

The magnitude of the magnetisation vector in the transverse plane depends on the duration of the r.f. pulse and hence the tip angle. If the pulse is on resonance and long enough to tip the z-magnetisation by 90° , M_{xy} is equal to M_z^0 . As the magnetisation vector rotates in the transverse plane, it induces an electric current in a wire that is coiled perpendicular to the static external magnetic field (Faraday's law). The decaying voltage is most commonly referred to as the Free Induction Decay (FID) and can readily be recorded using the r.f. receiver coil. In the receiver section of the NMR spectrometer, the NMR signal, which is in the order of μV , is amplified to a level where it can be digitised. The analogue-to-digital converter (ADC) then converts the signal into a binary number and it is stored in the computer. The ADC samples the signal at discrete time intervals t_d - the dwell time -, the frequency of which is determined by the highest frequency component f_{max} in the signal according to the Nyquist theorem:

$$t_d = \frac{1}{2f_{max}} \quad (2.13)$$

Furthermore, the NMR signal is acquired using a method called quadrature detection. This is the process of changing the phase of the receiver frequency to enable differentiation between the x- and y-component of the transverse magnetisation. These two components are then combined into a complex time-domain spectrum. Usually, the time-domain signal is subsequently transformed into the frequency domain using the Fast Fourier Transform (FFT) [67] to provide more information about the different frequency components and is the basis for further data analysis.

Looking at Equations 2.12a and 2.12b above, it can be seen that the T_2^* decay is what a receiver coil actually measures when a pulse-and-collect sequence is utilised. Both the spin-spin relaxation and loss of coherence due to magnetic field inhomogeneities (Equation 2.10) combined cause the transverse signal to decay. The observed linewidth of a signal in the frequency domain is associated with the time constant of signal decay. A relationship exists between the peak width at half height ($LW_{1/2}$) of a single resonance in the frequency domain spectrum and T_2^* . A representation of an absorptive Lorentzian line resulting from Fourier transformation of time domain data recorded with a pulse-and-collect experiment of a single resonant sample, e.g. water, is schematically shown in Figure 2.6.

Figure 2.6 Absorptive Lorentzian peak with indicated peak amplitude and $LW_{1/2}$.

The relationship between T_2^* and $LW_{1/2}$ in units of Hz ($\Delta\nu$) is given by

$$\Delta\nu = \frac{1}{\pi T_2^*} \quad (2.14)$$

The resolution of a NMR spectrometer is directly related to the minimum peak width that can be achieved. The smaller T_2^* , the faster the magnetisation decay in the transverse plane and the broader the observed signal. Line broadening can originate from the spectrometer itself causing large magnetic field inhomogeneities across the sample thereby increasing T_2' . This is the case when the magnet is not sufficiently shimmed or the NMR tube is not suitable (misshapen). The sample itself can also cause line broadening, for example if the sample is not homogenous or paramagnetic ions are present. Generally, these two options can be addressed by looking at the experimental setup, repeating the shimming and making sure that the sample is completely dissolved and well mixed. Large values of the compound inherent spin-spin relaxation, T_2 , can naturally also cause broad signals as is the case for very large molecules (slower tumbling when in solution) or solids, where chemical shift anisotropy results in the superposition of many resonances of slightly different frequencies. Attenuation of the spin-spin relaxation is widely used for the analysis of large biomolecules. However, this is not relevant to the work presented here and the reader is referred to the literature; an excellent review regarding enhancement of sensitivity in solution state NMR is given by Lee *et al.*[68].

Another effect of line broadening is a reduction in the signal-to-noise ratio of the resulting spectrum. Line broadening causes the signal amplitude to decrease because the integral area of any NMR resonance remains constant [12]. The noise in the spectrum remains unaffected and consequently, the sensitivity of the measurement is further reduced. This can become a significant issue when dealing with low concentrations and/or resonances from a sparse number of protons as well as when using low-field magnets. It is essential to ensure an optimal shim to ensure that magnetic field inhomogeneities do not accelerate T_2 relaxation, especially when low-field spectrometers are applied.

One option to enhance the SNR without changing to higher magnetic fields or increasing the sample concentration is signal averaging. The NMR signal itself is very weak and the signal from the probe is generally superimposed by random r.f. noise predominantly generated by the receiver coil. With a given spectrometer (hence changing the design of the hardware is not possible), only post-processing of the data and signal averaging can be used to increase the SNR. The former is most commonly done by means of multiplying the time domain signal with a weighting function before Fourier transformation. Application of weighting functions comes at the cost of spectral resolution due to the involved truncation of the FID — faster decay equals broader lines. Therefore, signal averaging is usually the most beneficial option for improvement of SNR unless time constraints, such as short sample lifetime, apply. Signal averaging exploits the fact that the NMR signal is repeatable whereas the noise varies randomly. If the same experiment — the simple pulse-and-collect to obtain a frequency domain spectrum — is repeated multiple times and the obtained spectra added together, the NMR signal will increase linearly with the number of measurements (commonly referred to as

"scans"). The noise signals on the other hand vary irreproducibly and are not correlated, hence simple noise averaging cannot be applied. The sum of noise signals from multiple experiments can be accessed by root-mean-square statistics and the following relationship can be derived:

$$SNR = \frac{signal}{noise} \propto \frac{s_{NMR}(1+2+\dots N)}{\sigma_{noise}(1+2+\dots N)} = \frac{N s_{NMR}(1)}{\sqrt{N} \sigma_{noise}(1)} = \sqrt{N} \frac{s_{NMR}(1)}{\sigma_{noise}(1)} \quad (2.15)$$

It can be seen that both the NMR signal and the noise increase with measurement repetition, but the NMR signal increases faster and this is exploited in signal averaging.

SNR enhancement through signal averaging can be very time consuming depending on the initial signal intensity and the required SNR as well as the T_1 of the sample. If the signal is not distinguishable from the noise with one scan, to essentially "pull" it out of the noise might require hours of experimental time. Furthermore, the repeated NMR measurements have to be separated by a time delay sufficiently long for the equilibrium along the z-axis to be fully restored — $\Delta t \gg T_1$ — in order to precisely repeat the experiment. Nevertheless, signal averaging is a useful tool to enhance the sensitivity of NMR measurements, especially with low-field NMR spectrometer where the instrument inherent sensitivity is much lower than in high field instruments.

2.2.4 Chemical Shift

The frequency domain spectrum of a sample, which is obtained using a simple pulse-and-collect measurement and application of the FFT to the time-domain data, plots adsorption intensity (vertical axis) versus frequency (horizontal axis) [67]. The number and position of the peaks that appear in this frequency domain spectrum can be used for compound identification and structure elucidation. In this context, it is important to discuss the concept of chemical shift.

Chemical shift is essentially the difference in Hz between any two resonances in a frequency domain spectrum. The chemical shift is influenced by the chemical nature of the molecule in which the nucleus resides. More specifically, the electronic environment of a nucleus displaces its Larmor frequency due to having an influence on the effective magnetic field that the nucleus experiences. Depending on the chemical bonds and the neighbouring nuclei, the electronic environment can be very different and hence the magnetic shielding effect is more or less pronounced. The effective magnetic field B_{eff} at the site of the nucleus is shifted from the applied magnetic field B_0 by a factor of σ :

$$B_{eff} = B_0 (1 - \sigma) \quad (2.16)$$

The nucleus precesses at a Larmor frequency that depends on the effective field B_{eff} rather than on the external magnetic field B_0 . Consequently, two protons of the same molecule will show distinct resonances in a frequency domain spectrum if their chemical (and hence electronic) environment is sufficiently different. For example, the proton in the OH-group and the protons in the

methyl(CH_3)-group of methanol give independent resonances in ^1H NMR. The distance between any two peaks of the same molecule varies depending on the strength of the applied magnetic field (can be seen from Equation 2.16).

The position of the signal of interest is commonly specified as its chemical shift δ_{ppm} , which is determined by comparing the resonance of interest to that of a reference compound. However, the distance in Hz between any two peaks is contingent on the strength of the applied magnetic field. To remove the dependence on the magnetic field strength, the chemical shift is a dimensionless number and commonly expressed in units of parts per million (ppm). The chemical shift of a nucleus appearing at frequency ν with respect to a reference compound at ν_{ref} is calculated via:

$$\delta_{ppm} = 10^6 \times \frac{\nu - \nu_{ref}}{\nu_{ref}} \quad (2.17)$$

Conventionally, tetramethylsilane (TMS) is used as the reference for ^1H nuclei with an arbitrarily assigned chemical shift of $\delta_{TMS} = 0$ ppm. Tabulated values for ^1H nuclei in different chemical environments are readily available. In practice, residual solvent signals or specifically added reference compounds at well defined frequencies can be used to determine the chemical shifts and enable identification of compounds in a spectrum.

Indirect interaction between directly and indirectly bonded nuclei via the surrounding electron clouds can be detected in NMR spectroscopy in terms of the spin-spin or J-coupling. This results in a further splitting of a resonance, for example a methyl-group splits the resonance of any ^1H coupled to the methyl-group with the splitting pattern being a quartet in this case. The combination of chemical shift and J-coupling provides a powerful tool for compound identification and structure elucidation using NMR. High magnetic fields and sufficient magnetic field homogeneity are necessary for this purpose in order to achieve the required chemical shift resolution. In the context of the work presented here, chemical shift resolution is used to differentiate between different compounds in the sample, further details, such as J-coupling, are not of interest.

2.2.5 Quantitative NMR

The inherent low sensitivity of NMR initially led to a lot of scepticism regards its application as a quantitative tool [69], but more recent progress in modern NMR techniques and the involved technologies and hardware has changed this perception. Today, NMR is routinely used as a quantitative tool [70] in the fields of chemistry, biology and medicine, e.g. for the purity analysis of drugs [71–74] or to determine the concentration and purity in the organic synthesis of natural products [75, 76]. According to Malz *et al.* [69], the linear relationship between peak intensity, or rather the integral peak area, and number of nuclei contributing to the peak makes NMR an excellent quantitative tool [69].

The most important relation of quantitative NMR (qNMR) is thus given by

$$A_x = K_s N_x \quad (2.18)$$

which describes that the integrated signal area A_x in a frequency domain spectrum is directly proportional to the number of nuclei N_x responsible for the resonance. K_s is a spectrometer constant. Most substances will show multiple resonances in a NMR spectrum according to the chemical structure; it is, however, sufficient to select one resonance and take into account the respective number of protons generating that resonance. Given a sample containing two different species x and y with distinct resonances, the ratio of the area integrals are directly proportional to the ratio of corresponding protons at resonance x and y :

$$\frac{A_x}{A_y} = \frac{N_x}{N_y} \quad (2.19)$$

Note that the spectrometer constant K_s cancels as the two species are exposed to the same experimental conditions.

Equation 2.19 allows for relative quantification of different species, isomers, diastereomers or enantiomers in the same sample. This is, for example, widely used in pharmaceuticals [77, 78]. The following relationship can be derived from Equation 2.19 to determine the molecular ratio n_x/n_y between two compounds x and y :

$$\frac{n_x}{n_y} = \frac{A_x N_y}{A_y N_x} \quad (2.20)$$

In a mixture with m compounds, the relative molar fraction of compound x is consequently assessed using

$$\frac{n_x}{\sum_{i=1}^m n_i} = \frac{A_x/N_x}{\sum_{i=1}^m A_i/N_i} \times 100\% \quad (2.21)$$

To achieve absolute quantification, a compound of known composition and concentration can be added to a sample as an internal reference. Thus equation 2.20 can be rewritten with the mass of the reference m_{ref} known to give m_x , the unknown mass of target analyte x :

$$m_x = \frac{A_x}{A_{ref}} \frac{N_{ref}}{N_x} \frac{M_x}{M_{ref}} m_{ref} \quad (2.22)$$

Herein, M_{ref} and M_x are the molecular weights of the reference compound and target analyte, respectively. Equation 2.22 can be further modified to determine the assay P_x of a compound weighed into the sample at known concentration and with a reference standard of known assay P_{ref}

$$P_x = \frac{A_x}{A_{ref}} \frac{N_{ref}}{N_x} \frac{M_x}{M_{ref}} \frac{m_{ref}}{m_x} P_{ref} \quad (2.23)$$

A suitable reference standard needs to satisfy the following requirements [79, 80, 76]

- No signal overlap; the reference resonance appears distinct from the target analyte
- Soluble in the solvent used for sample preparation
- Stable and chemically inert
- Inexpensive
- Ideally give one single, sharp line in the frequency domain spectrum
- Preferably shorter T_1 than the target analyte

The first criterion is crucial if accurate quantification shall be achieved. As can be seen from Equations 2.22 and 2.23, the integral area of the resonances of the references and the target analyte are extracted from the NMR spectrum to derive the target concentration. The integral area is directly proportional to the concentration and number of protons (at the resonance frequency) of the compound generating that peak. In order to accurately derive the concentration of the target analyte, the peak areas have to be established with high accuracy. Should two peaks appear close to each other in the frequency domain spectrum, such that they start to overlap, the respective integral areas cannot be determined correctly any more. Peak deconvolution can be applied to resolve two overlapping peaks, but this introduces additional uncertainty to the quantification. It is therefore essential to choose a reference compound that has a resonance distinct from any other resonance in the spectrum in order to enable determination of its integral area with high accuracy. Finding a universal reference standard proves to be an impossible task and each sample and target analyte has to be considered individually.

Further to using an internal referencing for quantitative analysis, other methods have been developed. This includes using an external standard in a concentric tube to achieve simultaneous measurement of both standard and sample [81, 82]. The reference standard can also be placed in a separate precision tube to enable quantification of the target analyte [83, 84]. For both cases, the reference and target analyte have to be dissolved in the same solvent and the volumes need to be accurately determined. Another approach, referred to as ERETIC (Electronic REference To access In vivo Concentrations), that uses an electronic signal to generate a pseudo-FID which provides the reference spectrum has been proposed in 1995 [85, 86]. To allow application of the ERETIC method, the spectrometer needs a free channel (heteronuclear) to feed the electronic reference signal to the probe. Amplitude, linewidth and the frequency are chosen by the operator, hence can be modified to suit the specific sample. However, calibration of the artificially generated reference signal against a standard of known concentration needs to be carried out before moving on to quantification of unknowns. PULCON - PULse Length Based CONcentration Determination - is another option for quantification measurements with NMR [87]. This method is based on reciprocity; the length of a π pulse in a given r.f. coil is inversely proportional to the attainable sensitivity [88, 89]. Further methods have been added to the list of external calibration methods, such as QUANTAS [90] — QUANTification by Artificial Signal —, ARTSI [91] — Amplitude-corrected Referencing Through Signal Injection — and PIG [92] — Pulse Into the Gradient — all of which use electronic reference signals (PIG is effectively an extension of the ERETIC method).

The focus of the work presented here is quantitative NMR analysis using the internal standard method in order to keep the requirements of the NMR hardware and measurement setup as simple and cost-effective as possible. Furthermore, the application of an external standard in a coaxial or second precision tube inevitably leads to loss of sample volume and hence decreased signal intensity. This can be a problem when looking at low target analyte concentrations, especially when low-field NMR spectroscopy is applied for the analysis and/or flow-through experiments conducted.

To achieve accurate and reliable quantification with NMR, the measurement has to be designed carefully and the parameters chosen according to the specific sample. A good SNR is essential to yield good resolution and accuracy. As mentioned above, the SNR is typically enhanced by repeating the pulse-and-collect sequence multiple times with the same sample. The applied repetition time T_R depends on the longest T_1 in the sample and the value being accurately assessed beforehand. If the spins have not returned to their equilibrium along the z-axis before subsequent excitation, the next pulse-and-collect sequence will produce a slightly different spectrum intensity associated with the different relaxation times in the sample. A value of $5 \times T_1 \leq T_R$ is routinely applied for quantitative measurements with NMR [93]. In addition to a long enough repetition time, the correct pulse length to achieve a 90° rotation of the magnetisation is desired in order to maximise the signal. Further important acquisition parameters include the acquisition time (long enough to avoid truncation of the FID), the number of time domain data points necessary for sufficient digital resolution of the signals (inversely related to the spectral width) and an optimal receiver gain (RG) to avoid baseline distortion and signal truncation (RG too high) and signal loss (RG too low).

In order to yield high resolution spectra with sufficient SNR, the magnetic field across the sample needs to be sufficiently homogenous. In this context, the most important parameter is the linewidth of the peaks, the $LW_{1/2}$ value in Hz. The minimum obtainable $LW_{1/2}$ is indicative of the spectral resolution as it defines how close two peaks can appear in a spectrum while still being distinguishable. As described by Equation 2.14, the linewidth is correlated to T_2^* and thus to magnetic field inhomogeneity effects that accelerate T_2^* relaxation (shorter FID). An insufficiently shimmed magnet causes inhomogeneity across the sample, thus the spins will lose phase coherence more quickly. The term "shimming" originates from the early days of NMR when field homogeneity of the large electromagnets was adjusted mechanically [94]. The poles of the magnets were moved relative to each other by turning bolts that held the pole faces. The fine tuning was then achieved by putting thin pieces of brass between the yoke and the pole pieces. These brass pieces were called *shim stock* and the process of placing them at the optimal location between the pole faces was referred to as *shimming*. Nowadays, instead of manually hammering metal pieces into the magnet support, the magnet probe is surrounded by coils which create small magnetic field when current is applied. The shimming process consists of tuning the current in these coils so that the magnetic fields they create either enhance or oppose the external field (active shimming). Typically, the shimming is automated in an iterative process to obtain the most homogeneous magnetic field across the sample. Evaluating

the resonance of a shim sample regarding the achieved linewidth, $LW_{1/2}$, indicates the quality of the shim. Usually, the shim sample is water or consists of a water and deuterated water mixture.

Broadening of spectral lines can also be caused by chemical exchange processes, that can be present as rapid jumping between possible molecular states or as an exchange of protons between two chemical species, e.g. the protons in a water molecule exchanging with that of a hydroxyl group. Depending on the time scale of the NMR experiment compared to that of the exchange rate, either two distinct peaks at the different Larmor frequencies (slow exchange rate) or a broadened peak at the average Larmor frequency (fast exchange rate) will appear. Chemical shift resolution is significant for detection of this phenomenon; it can only be observed at high field and a slow enough exchange rate. Additionally, chemical shift anisotropy and quadrupolar interaction can affect the relaxation mechanism and result in significant line broadening. However, these are not particularly relevant for the work presented here and will not be further discussed.

Further factors affecting the spectral lineshapes are the sample and sample tube itself as they can cause slight imperfections in the magnetic field across the sample through susceptibility effects.

After conducting the pulse-and-collect measurement with the sample plus reference standard of choice, post-processing is performed on the data. Prior to Fourier transformation of the time domain data, a window function can be applied to improve the SNR; this is often done with an exponential filter. However, windowing simultaneously results in line broadening of the signals and hence it is recommended to avoid windowing by achieving sufficient SNR through signal averaging [11]. Additionally, zero filling can be used to enhance the digital resolution. Data points with value zero are added; typically a factor of 2 is applied, hence doubling the number of data points. The FID must have decayed near to zero at the end of the acquisition time for this method to be effective. Nowadays, most spectrometer softwares are able to carry out zero filling and windowing in an automated procedure. After Fourier transformation, baseline correction and phasing of the frequency domain spectrum are performed. Both have a great effect on the accuracy of the results as they directly influence the integral signal areas. A variety of automatic baseline correction algorithms have been developed over the years [95–97] and most spectrometer softwares implement built-in baseline correction that can be applied easily and accurately. Manual phasing is generally preferred over automatic phasing [75] to avoid errors in smaller peaks. Here, too, algorithms to automate the phasing of spectra have been developed [98–100] and some of the available algorithms have also been evaluated comparing the accuracy and repeatability of the results [101]. The last step during processing of NMR spectra for quantitative analysis is integration of the signals of interest. The integral range has to be chosen wisely and consistently, especially in dense spectra or when other resonances are close by. Note that the operator is generally the main source of error in qNMR [69] and post-processing and analysis need to be performed carefully to yield accurate results.

To validate quantitative NMR measurements, accuracy, precision, linearity, and robustness have to be taken into account. Furthermore, the limit of detection (LOD) as well as the limit of quantification

(LOQ) are of interest. Accuracy of an analytical measurement is defined as the degree to which the measurement results conforms with the accepted true value or standard. Precision describes the closeness of a series of measurements, i.e. it indicates how well the results can be replicated in repetitive measurements under the same conditions. Both repeatability and reproducibility are closely related to precision. The variation in repeated measurements of the same sample under identical conditions is the repeatability whereas the variation in repeat measurements of the same sample under changing conditions is referred to as the reproducibility [102]. Accuracy can be assessed by measuring a known standard. Precision, hence repeatability and reproducibility, simply needs a homogenous sample to be measured in a few repetitions under stable and then varying conditions (operator, time, etc.). Due to the good electronic stability of NMR spectrometers, reproducibility is generally not an issue for qNMR measurements. The integral areas of a stable sample in a sealed NMR tube are reproducible with a variation less than 1 % over many years [103]. The linearity of a measurement protocol is usually established through the analysis of a series of dilutions of a standard followed by linear regression of the results. In this context, it is essential to select the concentration range of the standard solutions with respect to the conceivable range of the unknown samples to be measured. Another important validation parameter is the robustness of an analytical method. This indicates the degree to which the result changes when considerable, albeit small, changes are made to the analytical procedure. The parameters of data acquisition and processing can be changed systematically to assess the robustness of the qNMR measurements. Last but not least, the limits of detection and quantification are essential in qNMR — they define the minimum concentration of the target analyte that can be detected and quantified, respectively. The LOD and LOQ can be influenced by adjusting the experimental procedure and/or parameters, for example during sample preparation or data acquisition, as they depend on the SNR of the NMR measurement.

Validation of qNMR measurements has been performed routinely for a variety of applications, e.g. [70, 104–106]. There can be no universal validation for qNMR as it is dependent on the system used and the specific sample/s to be analysed, high-field versus low-field, multicomponent versus single-component, potential signal overlap, and so forth. Hence validation measurements have to be carried out for the specific application to provide proof of capability of the approach.

2.2.6 Low-field, Benchtop NMR

In recent decades, NMR spectroscopic analyses in the laboratory have been conducted using superconducting magnets [107]. The intrinsic low signal-to-noise ratio of NMR is overcome by establishing a homogeneous, high magnetic field across the sample to achieve high sensitivity and resolution. For structure elucidation and compound identification, the most common applications of NMR in laboratory settings are high field spectrometers with fields strengths of 7 T and above. The most powerful NMR spectrometer commercially available generates a 23.5 T magnetic field [108] and was first installed 2009 in Lyon's European Nuclear Magnetic Resonance Center. The other most

widely known application of NMR is as a body scanning procedure for medical purposes, this is known as Magnetic Resonance Imaging (MRI). Detailed 3D images of internal body structures can be generated using the protons that are present in both the water and fat in the human body, and clinical diagnostics can be conducted from the high tissue contrast provided. The standard in clinical MRI are field strengths between 1.5 and 3 T [109], ultra-high field magnets for whole-body MRI with 7 to 10.5 T field strengths are still limited to research applications [110] but will open up for clinical use, potentially with the speciality head scanners [111].

Strong magnetic field spectrometers are costly in acquisition, operation and maintenance, they are large in size and need dedicated NMR laboratories due to strong stray magnetic fields outside the actual spectrometer [112, 113]. Advancements in magnet design over recent years have opened up low magnetic field NMR spectrometers for applications where mobility, robustness to harsh conditions or low operating costs are necessary [114–116]. The definition of low-field can be arbitrarily chosen; in the context of the work presented here, the definition by Mitchell *et al.* [117] with low magnetic field being in the range of $B_0 = 10$ mT to 1 T is used. Instead of using cryoprobes, where the coil needs constant cooling to maintain the magnetic field it generates, permanent magnets are used for low-field spectrometers. The maximum field strength that can be achieved with a benchtop spectrometer featuring a permanent magnet is 1.5 - 2 T [118, 119]. In recent years, these spectrometers have seen growing interest and fields of application are still expanding. To build a closed magnet with a magnetic field as homogeneous as possible on the inside, the most commonly used design is the Halbach array, first proposed in 1980 by Klaus Halbach [120]. A schematic of the Halbach magnet configuration is shown in Figure 2.7.

Figure 2.7 Typical permanent magnet configuration in a cylindrical Halbach array where each magnet block has a slightly different polarisation than its immediate neighbour. The B_0 field is created inside along the z-axis. Shim and gradient coils (dark gray) can be included, the former belonging to the standard equipment of a benchtop low-field spectrometer. The sample is placed in a solenoid rf coil (light grey) which generates a B_1 field along the y-axis.

Small magnet blocks are arranged in a cylindrical pattern such that each block with its polarisation is slightly different to its immediate neighbours. Hereby, the stray field to the outside can be minimized while the homogeneity of the magnetic field on the inside is maximised. A different approach to construct a low magnetic field NMR spectrometer is the application of two parallel magnetic plates

mounted in an iron yoke where the magnetic field is induced between the two pole pieces [117]. Addition of gradient coils can allow more sophisticated measurements, such as imaging or diffusion, to be conducted. Both designs have been used to build NMR spectrometers for benchtop laboratory applications and are well-established for quality and process control in the food industry [121–124]. Further applications include low-field MRI [125, 126], reaction monitoring [127–129] and lie within the petroleum industry to measure asphaltenes [130], two-phase mixtures [131], emulsions [132, 133] or hydrates [134]. Alongside closed NMR spectrometers, open configurations are available that have the dedicated volume outside of the magnet and use the stray magnetic field for the measurement. The most prominent examples are well logging tools in the petroleum industry dating back to the 1950's [135, 117], Schlumberger introduced their first series of well logging tools in the 1970's. The industry standard in well logging are T_2 -relaxation measurements to yield information about the rock formation, such as porosity and water content. Another application of stray-field NMR instruments are portable, hand-held devices that can perform surface analyses on large samples. Well-established in this context is the NMR-MOUSE [136], which has been deployed to analyse cultural heritage objects [137, 138], to characterize polymer surfaces [139] or to study food system, e.g. oil-in-water emulsions [140].

A variety of experimental techniques are available for industrial applications of low-field NMR, of which the most commonly used are relaxation time measurements due to being less demanding with respect to magnetic field quality [114]. However, with the more recent improvements in field homogeneity and achievable sensitivity and resolution, low-field spectrometers can now be used for spectroscopy applications (although featuring lower chemical shift ranges) or to yield the more complicated 2D-spectra [115]. Furthermore, the use of hyperpolarisation techniques in combination with low-field NMR is explored to enhance the sensitivity and thereby expand the range of applications [141, 142].

2.2.7 Low-field NMR in the Oil and Gas Industry

In the oil and gas industry, NMR is predominantly applied in the form of well logging tools (see above). Research into using NMR for well logging began as early as the 1950's by Chevron and then Schlumberger. Despite no commercialisation of the early logging devices occurred, this research established the foundation for the principles of NMR well logging and data evaluation that are in use today [135]. Nowadays, NMR well logging tools are well-established amongst the other available devices (i.e. acoustic, gamma ray, resistivity) and enable characterisation of the formation in terms of pore structure, quantity of the fluids present therein and can even predict the fluid flow through the formation [143]. As the NMR well logging devices perform inside-out measurements, no spectroscopic information can be obtained. Rather relaxometry (T_1 and T_2) and diffusion measurements are conducted on the fluids which give indications of the properties and interactions with the surrounding formation [144]. Alongside well logging tools, NMR spectroscopy has also

found applications in the petroleum industry for compositional analyses of raw petroleum fluids and the derived products [145–147]. The methods developed for on-line application are numerous, a comprehensive summary is provided by Edwards [148]. On-line process controls are typically based on low resolution NMR spectroscopy and are established predominantly in refineries [149, 150] to optimize the process in real time. A variety of methods have been developed and validated that use high resolution NMR spectroscopy to analyse petroleum products providing convenient and fast results [151–153]. However, for applications in the field, low-field spectrometers have the advantage of robustness, size, price and ease-of-use.

Another emerging area for the use of NMR in the oil and gas industry is flow metering of multiphase oil-water-gas streams. A prototype was developed recently [154] using a pre-magnetisation coil, low-field permanent magnet and r.f. coil for detection to probe the process stream. This system uses T_1 relaxation to distinguish the phases. After successful testing in a field trial [155], the NMR flow meter has been made commercially available in 2015 (KROHNE Group) [156]. Further research is ongoing regarding the use of the earth's magnetic field in multiphase flow metering with NMR [157], which could potentially simplify the necessary hardware and make the measurement more flexible.

As mentioned above, process applications of low-field NMR to study crude-oil emulsions [158, 132, 133, 159] and hydrate formation [134, 160, 161] have been the focus of research in recent years (see Table 2.3). These studies provide the basis for optimisation of the process in terms of separation efficiency through investigations of emulsion stability with NMR, and flow assurance by looking into the mechanisms of hydrate formation in situ.

NMR has great potential in the oil and gas industry, specifically with respect to on-line or by-line applications of low-field NMR instruments in the field. However, given only recent technology improvements of low-field spectrometers, this is still an evolving field.

2.3 Solid-phase Extraction

Table 2.3 Example applications of low field NMR for the oil and gas industry. SSE = Stimulated Spin Echo, PFG-SE = Pulsed Field Gradient - Spin Echo.

Application	Technique & Field Strength	Capabilities
Droplet sizing of water-in-oil emulsions	CPMG, PFG-SE at 52 μ T / 0.5 T	Mean droplet size with accuracy of ≈ 10 %, low cost, mobile
Hydrate formation - shell growth measurements	SSE-PFG at 0.5 T	Determination of hydrate growth kinetic and water core size of opaque systems
Quantification of water and petroleum in biphasic mixtures	CPMG at 52 mT	Short experiment times of less than 5 min, non-destructive, reagents-free
Viscosity predictions for crude oil / crude oil emulsions	CPMG at 20 mT	Order of magnitude viscosity predictions over a wide range of emulsion viscosities, changes with temperature, non-destructive measurement, opaque systems
Quantitative multiphase flow characterisation	Pulse-and-collect at 52 μ T	Monitor stratified and slug multiphase gas / liquid flow, determine velocity distributions
Clathrate formation and dissociation processes	CPMG at 50 mT	Dynamic molecular information of the hydrate phase and the coexisting liquid phase during hydrate transition

2.3 Solid-phase Extraction

Solid-phase extraction (SPE) is a well-established sample preparation technique to extract and/or pre-concentrate target analytes from liquid bulk samples for analysis. SPE is also used for removal of interferences or contaminants prior to analysis and, to a lesser extent, for sample storage [162]. In SPE, a liquid (most commonly aqueous) sample is passed through a solid sorbent material whereby the target analyte interacts with the sorbent and is retained in the material. Subsequently, the target is eluted from the sorbent with a solvent of sufficient strength. The obtained extract (target analyte in the solvent) is then measured with the method of choice. SPE was developed to complement the more traditional liquid-liquid extraction (LLE), but has evolved to be the predominantly applied technique of the two [163]. In LLE or solvent extraction, the analyte of interest is transferred between two immiscible, liquid phases according to its relative solubility. The reversible distribution reaction of analyte X between two phases A (sample) and S (solvent) and the respective distribution coefficient is

given by [164]

$$X_A \rightleftharpoons X_S$$

$$K_D = \frac{[X]_S}{[X]_A} \quad (2.24)$$

Herein, the brackets denote the concentration of analyte X in the respective phase. Thus, extraction into the solvent can only occur when the distribution coefficient is large. The solubility of X in S must be greater than in A.

Reduced solvent consumption, higher reproducibility and recovery factors as well as reduced time and cost when compared to LLE outline the benefits that have caused SPE to become the preferred sample preparation technique [165, 166]. Furthermore, multiple extractions can be run in parallel and the process can be readily automated [167].

Figure 2.8 Schematic of the basic procedure for reversed-phase SPE applying four steps (1) Conditioning (2) Loading (3) Washing and (4) Eluting. For each step, two images are showing presenting its start (left) and end (right).

The solid-phase extraction procedure typically consists of four steps as shown schematically in Figure 2.8 and described here in more detail:

1. Conditioning

The conditioning step prepares and wets the sorbent for the extraction procedure to guarantee immediate and effective contact with the analyte of interest. Usually, a small volume of a polar, organic solvent (methanol or acetonitrile) is passed through the sorbent material whereby the surface becomes more hydrophilic [165]. Without conditioning, the majority of the available SPE sorbent materials lose some of their retention capability. However, sorbent materials have been developed where conditioning can be omitted [163] due to better wettability [163, 168]. Conditioning the sorbent also removes potential impurities from the manufacturing process.

2. Loading

The liquid, most commonly aqueous, sample is passed through the sorbent material with the help of a pump (inlet) or vacuum (outlet). The flow rate needs to be constant and selected according to the size of the sorbent particles. Sufficient interaction time between the sorbent and the analyte of interest for maximum retention must be ensured, hence SPE is often associated with low flow rates.

3. Washing

Loading is commonly followed by a washing step, where a wash liquid is passed through the sorbent without eluting the target analyte. This is done to remove any impurities, salts or non-extracted materials. The most common application of SPE is the extraction of organic materials from aqueous bulk samples and in this context, water is the wash liquid. However, additives, such as low concentrations of organic solvents, can be used to increase the clean-up efficiency of this step.

4. Elution

The last step in the SPE procedure is eluting the target analyte from the sorbent material with a solvent. Solvent selection has to be made according to the sorbent material, target analyte and the subsequent analytical method. If the selected solvent is immiscible with water, it is recommended to remove the residual water from the sorbent material before elution to avoid contamination of the subsequently extracted sample.

2.3.1 SPE Mechanisms

Three traditional types of SPE mechanisms can be distinguished: normal-phase, ion-exchange and reversed-phase. Polar sorbents are used in normal-phase SPE that adsorb polar analytes from a nonpolar sample matrix. The earliest application dates back to the beginning of the 19th century, when Twsett separated chlorophyll from a light petroleum mobile phase using a polar calcium carbonate column [169]. Polar forces including (induced) dipole-dipole interactions, hydrogen bonding and π - π electron interactions induce the retention of the polar analyte. Desorption of the analyte is carried out with a solvent of high elution strength that disrupts the interactions. Silica, alumina, magnesium silicate (Florisil), and bonded silica sorbents with attached highly polar functional groups are most commonly used in normal-phase SPE [164]. Typical applications are clean-up procedures of organic extracts or the fractionation of petroleum hydrocarbons. Ion-exchange SPE is used when the analyte of interest is ionised (positively or negatively charged) or can be ionised by pH adjustment when in solution. In this case, the sorbent material contains ionised functional groups. The charge of the sorbent functional groups is opposite to the charge of the analyte in solution, so that electrostatic or ionic bonds effect the retention. Anion exchange involves a positively charged sorbent interacting with a negatively charged analyte. In cation exchange SPE, the sorbent is

negatively charged whereas the analyte is positively charged. Ion exchange sorbents can be based on apolar polymeric resins or bonded silica sorbents. To elute the analyte from the sorbent material, a solution with a pH that neutralises either of the functional groups is applied. Another option is to use a solvent that has a high ionic strength. Van-der-Waals forces between the target analyte and the functional groups of the sorbent material induce the retention in reversed-phase SPE. The interactions are comparatively weak; no chemical bond is formed and the retention depends primarily on the molecular structure. In general, this implicates poor selectivity making reversed-phase SPE the method of choice for complex samples where the analyte of interest consists of a range of compounds. Established sorbents for reversed-phase SPE include surface modified silicas [170] — hydrocarbon chains attached to the silanol groups of a silica base —, porous polymers [163] and carbon [171]. In addition to the traditional types of SPE and the respective sorbent materials, more selective sorbents have emerged using molecular recognition (affinity), restricted-access matrix or covalent bonding to retain analytes.

2.3.2 Method Development

Selection of the appropriate sorbent and hence SPE mechanism is typically made according to the nature of the target analyte and its structure. An example of a guide that can be used to select a suitable sorbent for an organic target analyte is shown in Figure 2.9 below.

Figure 2.9 Selection guide for solid-phase extraction of organic analytes from solution. SAX = Strong Anion Exchanger, SCX = Strong Cation Exchanger, SCX = Weak Cation Exchanger, RP = Reversed-Phase, NP = Normal-Phase, IE = Ion-Exchange. Replicated based on [172].

It is important to note that the selection guide in Figure 2.9 provides only a starting point, the fine method selection usually evolves empirically [172]. Two essential parameters when developing a solid-phase extraction protocol are the recovery and the breakthrough volume. The former depends

on the retention efficiency of the sorbent and the elution ability of the solvent. It is calculated as the product of sorption efficiency (retention) and desorption efficiency (elution). The breakthrough volume is the maximum sample volume that can be passed through a sorbent material of defined size and weight with 100 % retention of the target analyte. The breakthrough volume is experimentally determined by loading the sorbent with the sample and monitoring the fluid at the exit with respect to target analyte concentration. The point at which an arbitrary amount of the target analyte is detected at the outlet is the breakthrough. The breakthrough volume is typically used to assess the suitability of a developed method for the intended objective SPE and to determine the retention capacity of the sorbent.

The sorbent material is selected based on the chemistry of the sample matrix and target analyte. Furthermore, selectivity has to be considered; the goal is to retain all of the target analyte while any impurities or interferences pass through. Both the size of the particles and bed weight play a significant role in terms of retention capacity as they determine how much of the analyte can be "stored" in the sorbent matrix. To maximise the breakthrough volume and hence retention capacity, the sorbent bed should be large. However, large sorbent beds require more solvent and result in enhanced dilution of the target analyte. In general, the smallest sorbent bed possible should be used. Another consideration with respect to the sorbent is the format of the SPE device — a large variety of commercially available formats exists, such as cartridges, columns, disks, pipette tips, well extraction plates and more.

The solvent selected for elution needs to be strong enough to disrupt the interactions between the sorbent and target analyte and it must be compatible with the selected method for analysis. As a rule of thumb, the elution volume should be 2 - 5 times the sorbent bed volume [171].

Once the sorbent material, format and solvent are selected, the method can be trialled and optimised. The optimum loading volume has to be determined whereby the breakthrough volume as well as the required extent of pre-concentration have to be considered. The minimal volume of solvent has to be defined that recovers the maximum of the target analyte from the sorbent. The flow rate is usually specified by the manufacturer of the selected SPE sorbent, but should be tested and where applicable, adjusted to yield maximum recovery.

2.3.3 SPE for Analysis of Hydrocarbons in Water

Oil and grease analysis of aqueous samples conventionally uses liquid-liquid extraction (also referred to as solvent extraction) as the sample preparation technique. The official reference methods defined by the United States Environmental Protection Agency (US EPA) [33] and by ASTM International [173] for the determination of oil and grease in water and wastewater both detail LLE for sample preparation. Despite research showing that SPE has advantages over LLE in terms of higher recovery and reproducibility for various other applications (for example in food analysis [174] or determination

of pesticides in water [175, 176]), SPE has not replaced LLE for hydrocarbon extraction from water for oil-in-water measurements yet. US EPA Method 1664A does allow SPE to be used for sample preparation under the condition that it can be demonstrated to yield results that are equivalent to those obtained with LLE. However, commercially available instruments certified for the oil and gas industry to provide quantitative analysis of hydrocarbons in produced water predominantly use LLE to extract the hydrocarbons from the water matrix [177, 178]. Because of the prevalence of LLE as the sample preparation method in the oil and gas industry and an apparent lack of effort to implement changes to seemingly working systems, SPE has not had a breakthrough for this application yet.

The field of SPE for extraction of organic compounds is widely researched and a variety of methods have been established. A comprehensive summary and critical review can be found in [179] and [180]. SPE for the isolation of polycyclic aromatic hydrocarbons from different sample matrices in environmental analysis is also very well established [181]. However, the application of SPE to specifically extract oil and grease, hence aromatic and aliphatic hydrocarbons, from water remains a largely unresearched field with only a few studies so far conducted in the 1990's. Wells *et al.* [182] compare SPE with commercially available EnvirElut columns, LLE and a continuous LLE (CLLE) procedure for the determination of oil and grease content in water. They observed that their developed two-stage SPE procedure compares favourably with both LLE and CLLE providing consistent results, specifically for the environmentally contaminated samples under investigation. Lau and Stenstrom [183] performed a similar study also using commercially available SPE materials (chemically bonded silicas) for oil and grease analysis. C2, C8 and C18 attached to a silica backbone were considered, of which C18 was singled out to provide the highest recovery. This was subsequently compared to LLE and again, it was pointed out that SPE yielded higher recovery factors and prevented the loss of the volatiles. The authors concluded that SPE showed great potential for oil and grease analysis.

In the research presented in this dissertation, the objectives of using solid-phase extraction are isolation of hydrocarbons from water, pre-concentration and transfer into a solvent compatible with quantitative NMR analysis. In this context, the target analytes are both aromatic and aliphatic hydrocarbons dispersed and dissolved at the ppm level in water. Using the selection guide in Figure 2.9 as well as the results from previously conducted research [183, 182], reversed-phase SPE with chemically bonded silica forms the basis of the research. Initial measurements for sorbent selection as well as the detailed method development are outlined in Chapter 3.

Chapter 3

SPE-NMR Proof of Concept

This chapter introduces the application of quantitative ^1H NMR analysis in combination with solid-phase extraction to determine the oil-in-water content of produced water and demonstrates its proof of concept. Section 3.2 details the NMR measurement in terms of the instrument chosen and specifics of the experimental procedure. This is followed by a description of the SPE process and method development in Section 3.3. Then, information about the alternative, well-established methods that are deployed for measurement validation is given in Section 3.4. The specific sample preparation and preliminary validation measurements are detailed in Sections 3.5 and 3.6, respectively. The application of solid-phase extraction (SPE) to extract hydrocarbon contamination from water is compared to the more conventional liquid-liquid extraction (Section 3.7) to substantiate its feasibility. The proposed approach, SPE in combination with low-field ^1H NMR, is then deployed to determine the hexane (Section 3.8) and crude oil (Section 3.9) content of contaminated water samples and the measurements validated against alternative methods. Lastly, the SPE procedure for crude oil isolation from an aqueous bulk matrix is optimised with respect to the deployed sorbent material and experimental parameters (Section 3.10). Section 3.11 summarises the findings and provides an outlook with respect to subsequent work.

3.1 Background

Although NMR spectroscopy has found some application in the petroleum industry for process control and optimisation, it has not found its way into the field of produced water analysis yet. Other methods, predominantly infrared and gas chromatography for laboratory analysis as well as infrared and UV based methods for field applications, are well-established. Neither the operators of oil and gas platforms nor vendors of oil-in-water sensors seek to invest time and money into new technology. Efforts focus predominantly on improving already developed methods. Furthermore, a lot of progress has been made regarding subsea processing and separation of oil from produced water. Nevertheless,

a technology gap remains in terms of subsea OiW measurements to allow direct discharge of the separated water stream at the wellhead [184]. In this context, the technologies that are seen with the greatest potential for subsea, on-line monitoring are laser induced fluorescence (LIF), imaging and light scattering [184, 46]. These technologies are all optically-based and most efforts are focussed on optimising the sensor cleaning mechanisms and improving the robustness to the harsh subsea conditions.

In the context of quantitative produced water analysis in the field, the feasibility of using solid-phase extraction in combination with quantitative NMR analysis at low magnetic field is explored. The ultimate scope of the application is subsea, but the sensor shall also be suitable for benchtop laboratory analysis as well as onshore and offshore in-field utilisation. In a primary step, an appropriate methodology is developed and the suitability of the approach shown through laboratory measurements. Establishing a suitable methodology for the SPE procedure and subsequent NMR analysis follows and proof of concept with respect to deploying it for OiW monitoring is provided.

3.2 NMR Instrumentation and Measurement

Despite the high sensitivity and excellent resolution obtainable with high-field NMR spectrometers, their application is not feasible in the context of an OiW monitor due to size, cost and sensibility to varying surrounding conditions. Low-field NMR spectrometers feature low cost, mobility and robustness which makes them suitable for field deployment. In the context of this doctoral research, two benchtop ^1H NMR spectrometers with a magnetic field strength of 1 Tesla were used.

3.2.1 NMR Spectrometers

For the initial measurements and proof of concept, a preproduction model of the now available commercial benchtop system from Magritek Ltd., New Zealand, was used. The ^1H NMR hardware consists of an ultra-compact (8 kg) Halbach array magnet with a field strength of 1 Tesla and a Kea spectrometer, hereafter referred to as the *1 Tesla*. Figure 3.1a shows the magnet and its dimensions.

The magnet has a ^1H resonance frequency of 43.36 MHz and accommodates standard glass NMR tubes with 5 mm outer diameter (OD). The Halbach array is able to provide sufficient field homogeneity for chemical shift resolution with a minimum obtainable linewidth $LW_{1/2}$ of approximately 4 Hz (water peak). The system is equipped with a custom-built gradient coil that facilitates diffusion measurements (this feature is not used in the work presented here). For temperature control, the magnet is located inside a climatic chamber and the temperature kept constant at 27.1 °C. All measurements for the proof of concept were performed on the 1 Tesla (T).

During the course of this doctoral research, a self-contained benchtop NMR spectrometer was purchased for the OiW measurements and replaced the 1 Tesla. The *Spinsolve* is the advanced,

Figure 3.1 Benchtop ^1H NMR spectrometers built by Magritek. (a) Prototype of a 43 MHz (1 Tesla) system and (b) Spinsolve benchtop system with a magnetic field strength of 1 Tesla corresponding to 43 MHz proton resonance frequency.

commercial version of the 1 Tesla (available since 2013) and was also developed by Magritek Ltd., New Zealand. The model used for OiW monitoring is the Spinsolve 43 which operates at a proton resonance frequency of 43 MHz. A photo of the spectrometer can be seen in Figure 3.1b. The hardware including the magnet (also designed in the form of a Halbach array), amplifier and a temperature control is contained within the housing rendering the Spinsolve self-contained at a weight of 55 kg. To run measurements, only power and a laptop are required. The built-in temperature control keeps the magnet temperature constant at $28.5\text{ }^{\circ}\text{C}$, the average surrounding temperature should be in the range 19.5 to $25.5\text{ }^{\circ}\text{C}$ to yield optimal system performance. The stray field around the system is $< 0.2\text{ mT}$ (2 Gauss). The 5 Gauss line, which is the perimeter around the NMR magnet with static magnetic fields higher than 5 Gauss, is completely contained in the system. 5 Gauss and below are considered safe in terms of the strength of the static magnetic fields present. The spectrometer can be run with an easy-to-use software that provides a variety of pre-defined measurements or with a more advanced software, which allows the modification of a wider range of parameters and running user programmed scripts.

Compared to the 1 Tesla, the Spinsolve features improved sensitivity and resolution achieving a linewidth $LW_{1/2}$ of below 0.7 Hz with a standard calibration sample of 10 % v/v $\text{H}_2\text{O} / \text{D}_2\text{O}$ (water in deuterium oxide). Shimming the magnet is typically done with the standard calibration sample (10 % v/v $\text{H}_2\text{O} / \text{D}_2\text{O}$); a simple water sample can be used as well. Manual shimming can be performed using the expert software, but the automatic shimming procedure (option provided by both software packages) readily achieves the linewidth as specified by the manufacturer. Potential drifts of the magnetic field strength while running measurements are corrected automatically using a fluorine

NMR lock that is integrated into the magnet probe. This corrects the magnetic field through an independent lock circuit, measuring and comparing the frequency of the lock signal. Magritek offers gradient coils that can be added to the Spinsolve to extend the variety of available measurements. The family of Spinsolve spectrometers has been developed further and also provides more sophisticated packages, such as multi nuclear NMR spectrometers or a combination of enhanced resolution and integrated solvent suppression. However, for the purpose of an automated OiW measurement for in-field application, the basic Spinsolve with a single proton channel and no additional features is selected to minimize the equipment and electronics.

Similar to the 1 Tesla, the Spinsolve accommodates standard NMR tubes with 5 mm OD. As the sample bore extends all the way through the magnet, the Spinsolve can also be used for on-line NMR measurements with a tube running through the magnet.

3.2.2 SPE and Quantitative NMR for Oil-in-water Analysis

The conceivable concentration of oil in produced water is at the ppm level, for environmental compliance it needs to be at maximum 30 mg/L. This poses sensitivity challenges in terms of analysis with low-field ^1H NMR. Due to relatively small chemical shift differences between the water and the aliphatic hydrocarbon resonances, the peaks overlap. The oil resonance will effectively disappear underneath the water peak because of its low concentration. Thus, it is necessary to pre-concentrate and extract the hydrocarbons from the aqueous phase using a suitable solvent. The extract can then be transferred to the low-field ^1H NMR spectrometer for analysis using a simple pulse-and-collect measurement. The combination of solid-phase extraction for sample preparation and pre-concentration and subsequent application of quantitative NMR analysis is referred to as SPE-NMR in the context of the work presented here. The development of the extraction procedure using reversed-phase SPE is discussed further below in Section 3.3. At this point, the elution solvent is described in more detail due to its significance for the NMR measurement.

A solvent has to be selected that recovers the contamination from the SPE sorbent but is also suitable for the subsequent measurement, hence it shall provide a reference signal to enable quantification of the target analyte oil. Using the bulk solvent as the reference would produce a ratio of oil to solvent signal intensity that is diminishingly small considering the low concentration of oil present. Consequently, it was decided to use a bulk solvent giving no resonance in ^1H NMR and add a reference compound at low concentration. The reference compound is required to produce a single, sharp resonance well separated from that of the oil. Crude oil composition can vary significantly with source and age, hence it does not have a characteristic, constant chemical shift. Furthermore, the complex composition of crude oil causes peak broadening and, generally, more than one peak can be expected. Figure 3.2 below shows typical frequency domain spectra of a light crude oil and a condensate measured with at a proton resonance frequency of 43 MHz.

Figure 3.2 Frequency domain spectra of (a) a light crude oil and (b) a condensate obtained with low-field ^1H NMR spectroscopy.

The spectra shown in Figure 3.2 have similar features. The dominant peak is a multiplet with a chemical shift of approximately $\delta = 0.9 - 1.4$ ppm. Around $\delta = 7$ ppm, a very broad resonance with low amplitude is discernible. The dominant peak is a doublet in the case of the light crude oil and a triplet for the condensate. The condensate spectrum shows a few smaller resonances that are not visible in the crude oil spectrum. For both compounds, the multiplet at $\delta = 0.9 - 1.4$ ppm can be assigned to the methyl- and methylene-groups of the aliphatic hydrocarbons. It is not possible to enhance the resolution of peaks with low magnetic field because they are the result of a range of hydrocarbons that vary in length and extent of branching. The broad, small resonance around $\delta = 7$ can be attributed to aromatic hydrocarbons present in the crude oil and condensate. Compared to the amount of aliphatic hydrocarbons, the aromatics represent a significantly smaller fraction of the total petroleum hydrocarbons ($< 1\%$). Naturally, crude oils exist with a much higher fraction of aromatic hydrocarbons and/or significant parts of other hydrocarbons, such as alcohols or acids, that will inevitably result in additional peaks and more complex spectra. Initially however, for method development and proof of concept, only aliphatic crude oils with negligible amounts of aromatic hydrocarbons will be considered.

As discussed above, an organic, polar solvent that provides the bulk liquid in which the actual reference is dissolved and that does not interfere with the measurement is required. An appropriate option is perchloroethylene (PCE), also known as tetrachloroethylene. It is a strong organic solvent and, with no protons in its structure, does not show a resonance in ^1H NMR. Using PCE as the base solvent, a reference compound with a single resonance sufficiently separated from the aliphatic resonances between $\delta = 0.9 - 1.4$ ppm at a magnetic field of 1 Tesla is needed. TMS, the conventionally used reference for ^1H nuclei, is not suitable in this context because of its low boiling point. Of other commonly used NMR reference standards with higher boiling points, hexamethyldisiloxane HMDSO ($\delta = 0.07$ ppm) or dichloromethane DCM ($\delta = 5.33$ ppm) [185], were considered as potential reference compounds. However, the frequency separation of their peaks

from the methyl- and methylene-resonances in a magnetic field of 1 Tesla — 170 Hz for DCM and 35 Hz for HMDSO — is not deemed sufficient. Chloroform (CHCl_3), with a chemical shift of $\delta = 7.26$ ppm [185], provides a separation of ≈ 250 Hz and was chosen as the compound with the highest potential as a reference to quantify oil contamination. The chloroform is added at 1% v/v to the PCE solvent in order to give a reference peak with similar intensity as is expected from the oil peak (after SPE). A typical spectrum of crude oil in the solvent system of 1% CHCl_3 in PCE after SPE is shown in Figure 3.3.

Figure 3.3 ^1H NMR spectrum of crude oil in a solvent consisting of PCE with 1% v/v CHCl_3 . 1 — resonance of CHCl_3 . 2 — resonance of aliphatic hydrocarbons (crude oil).

Separation of the hydrocarbon peaks (peaks 2) and chloroform (peak 1) is excellent and the peak intensities are of similar magnitudes, thereby enabling reliable area calculation for each of the peaks.

After data acquisition, application of FFT and post-processing, the obtained frequency domain spectrum (such as the one shown in Figure 3.3) can be analysed to quantify the oil content. General quantitative NMR analysis was discussed in detail in Chapter 2.2. The relevant equation to extract the mass of a target analyte with known composition from a frequency domain spectrum in the presence of a reference compound of known composition and mass is given by Equation 2.22. The equation is repeated here for convenience:

$$m_x = \frac{A_x}{A_{ref}} \frac{N_{ref}}{N_x} \frac{M_x}{M_{ref}} m_{ref} \quad (2.22 \text{ revisited})$$

Herein, A_x and A_{ref} are the integrated signal areas of the target analyte and reference compound, respectively, and M_x and M_{ref} are the respective molecular weights. The number of hydrogen nuclei in the target analyte and reference compound, respectively, are N_x and N_{ref} . The mass of the reference compound is m_{ref} , whereas m_x is the mass of the (unknown) target analyte.

For this equation to be applicable, the composition of the target analyte in terms of molecular weight and the number of hydrogen nuclei at the considered resonance need to be known. However, when crude oil, natural gas or condensate is the target analyte, the number of protons per molecule is generally unknown as is the molecular weight. Instead, the hydrogen index (HI), defined as the amount of hydrogen in the respective compound relative to the amount in water [186], can be used. Equation 2.22 is consequently modified to give:

$$m_x = \frac{A_x}{A_{ref}} \frac{HI_{ref}}{HI_x} V_{ref} \rho_x \quad (3.1)$$

The hydrogen indices HI_{ref} and HI_x of the reference compound and crude oil, respectively, need to be determined separately. In the case of a specific compound where the number of protons is a known quantity, i.e. for the reference compound chloroform, the HI can be calculated according to [186]

$$HI_{ref} = \frac{\rho_{ref} N_{ref}}{M_{ref} * 0.111} \quad (3.2)$$

where ρ_{ref} is the density of the reference compound chloroform and the value of "0.111" originates from the proton density in pure water ($\frac{\rho_{H_2O} N_{H_2O}}{M_{H_2O}}$). The hydrogen index of crude oil can be approximated with the following equation [187]:

$$HI_x = 9 \rho_x (0.15 + 0.2(0.9 - \rho_x)^2) \quad (3.3)$$

Herein, the density of the crude oil ρ_x is usually known for a given reservoir or an approximate value can be deployed according to the assumed composition of the oil. Note that Equation 3.3 is an empirical formulation derived from the relationship of density and hydrocarbon index for a variety of hydrocarbons. In the case of heavy crude oils with elevated content of aromatics and polyaromatics, this correlation will not be able to estimate the hydrogen index adequately. Instead, it is advised to use alternative correlations developed by Kleinberg and Vinegar [188] that capture the reduction in HI for crude oil with an API gravity of 25 or lower.

For the light, mostly aliphatic crude oil used in the context of the work presented here, the combination of Equations 3.1, 3.2 and 3.3 yields the oil concentration in the solvent given the presence of a suitable reference, i.e. chloroform.

3.2.3 NMR Measurement

Proof-of-concept NMR measurements were performed on the 1 Tesla system. The pulse sequence consisted of a standard pulse-and-collect experiment. The π r.f. pulse with -15 dB amplitude was applied for 5.5 μ s. To enhance the SNR, the measurements were averaged over 128 scans with a repetition time T_R of 15 s, thus resulting in an acquisition time of 32 min for one measurement. The

parameters of the pulse-and-collect sequence were kept constant throughout all measurements. T_R was chosen based on the longest potential longitudinal relaxation time present. The T_1 values of hexane (as a model compound for aliphatic crude oils), an aliphatic crude oil and chloroform in PCE were assessed in a separate measurements through inversion recovery. Of these, the chloroform at 1 % v/v in PCE presented the longest T_1 at 2.1 s ($T_{1,hex} = 2s$ and $T_{1,oil} = 0.7s$) and hence the chosen repetition time of 15 s fulfils the requirement of $5 \times T_1 \leq T_R$. Note that the number of scans and resulting measurement time are specific to the 1 Tesla. This can be significantly reduced when the Spinsolve is applied instead due to its improved sensitivity and better magnetic field homogeneity.

3.3 SPE Methodology

The development of a suitable method for solid-phase extraction of aromatic and aliphatic hydrocarbons from a water matrix followed a mostly empirical approach. The starting point to select suitable sorbent materials is usually the chemistry of the sample and analyte of interest. In the context of the work presented here, the bulk sample matrix is water and the analyte of interest covers a range of hydrocarbons, both aromatic and aliphatic. According to the selection guide presented in the previous chapter (see Figure 2.9), reversed-phase SPE is suggested. In comparison with the other types of SPE, reversed-phase SPE presents lower selectivity and weaker interaction forces. However, this is advantageous when dealing with complex samples where the analyte of interest is not one specific compound. When the aim is the extraction of a range of hydrocarbons from water, poor selectivity is desired. Another pre-requisite is the utilization of a commercially available product to guarantee accessibility at low cost.

The majority of manufacturers providing SPE supplies provide a selection and method development guide [189–191]. From these it can be deduced that chemically bonded silica sorbents qualify for the extraction of hydrocarbons from water. Chemically bonded silicas are generally specified by the length of the hydrocarbon chains attached (e.g. C2, C4, C8), carbon loading in percent, particle size and endcapping/non-endcapping. The length of the hydrocarbon-chain influences the size of the molecules that are preferably retained. Shorter chains are better for large molecules due to less steric hindrance. The parameter that is closely related to the retention capacity of silica based sorbents is the carbon loading. It defines the density of the hydrocarbon-chains on the silica base and thus specifies the surface coverage. A higher percentage of carbon loading indicates higher capacity of the sorbent. This can be explained with the transfer process of the target analyte from the sample to the sorbent. The transfer is dominated by partitioning [192], where the affinity of the analyte for the sorbent molecules, the hydrocarbon chains, is the driving force. Hence more hydrocarbon chains indicate more capacity to retain target analytes. The properties of the sorbent also differ for endcapped and non-endcapped silicas. After the hydrocarbon chains are attached to the silica base during synthesis, unreacted silanol groups will remain on the silica base and provide

potential sites for unwanted chemical bonding. Endcapping is the process of reacting those residual silanol groups with a capping agent such as trimethylsilylchloride. This renders the sorbent non-polar and less prone to degradation in harsh conditions. The schematics in Figure 3.4 show some examples of the structure of silica based sorbents including the difference between endcapping and no endcapping.

Figure 3.4 Chemically bonded silica sorbents for reversed-phase SPE where hydrocarbon chains are attached to the silica base. Shown are schematics of the structure of (a) octyl bonded silica, (b) phenyl bonded silica, (c) octadecyl bonded silica and (d) octadecyl bonded, endcapped silica.

For the initial measurements to show the feasibility of SPE in combination with quantitative NMR for OiW analysis, a readily available SPE cartridge with an octadecyl bonded, endcapped silica sorbent was chosen. The cartridges named Prevail™, were obtained from Grace (Columbia MD, United States *now distributed in Australia by PhaseSep Pty Ltd*). They have a carbon loading of 11 %, an average particle size of 50 μm and a bed weight of 900 mg. The Prevail cartridges were chosen on the basis of rudimentary first measurements confirming that they are able to retain an aliphatic crude oil. The cartridge housing provides luer hubs (see Figure 3.5 below) that aid in the setup of an automated measurement protocol by means of a simple slip connection between the male part on the cartridge and a female counterpart from the pump line. Furthermore, the sorbent does not need conditioning as per manufacturers recommendations. However, during the proof of concept measurements discussed in this chapter, the SPE material was conditioned to allow initial assessment of the general applicability of the selected sorbent. Further development and optimisation of the SPE procedure is detailed below.

SPE-NMR Proof of Concept

According to the standard reversed-phase SPE procedure with chemically bonded silica sorbents (refer to Figure 2.8 for a schematic of reversed-phase SPE), conditioning is performed with a polar solvent and a liquid that resembles the bulk phase of the sample. Consequently, the cartridges were conditioned with methanol and deionised water, typically 10 ml of each liquid were applied. An Ismatec REGLO-ICC four channel peristaltic pump provided a constant flow rate of 5 ml/min for conditioning, sample loading and elution (refer to Figure 3.5 for a schematic of the experimental procedure). A flow rate of 5 ml/min is the maximum rate recommended by the manufacturer that allows sufficient time for interaction between the sorbent and the target analytes.

Figure 3.5 Experimental procedure for solid-phase extraction using Prevail™ SPE cartridges. (1) Conditioning solvent (2) Sample loading (3) Compressed air (4) Eluting solvent.

The typically expected concentration of oil in the aqueous phase is around 30 mg/L or preferably lower, depending on the local environmental regulations for discharge water. The retention capacity of the cartridges is specified by the manufacturer to be 45 mg. This describes the total amount that the sorbent can bind, the exact value will vary with sample and target analyte(s). Given these factor, the loading volume was set to 250 ml, hence providing a safety margin regarding the retention capacity. Via analysis of the effluent water exiting the cartridge, the chosen loading volume and flow rate were shown not to saturate the sorbent.

It is common practice to include a washing step before elution (step (3) in Figure 2.8) to remove any unwanted species from the sorbent that might interfere with the subsequent analysis (refer to general guides on SPE method development, e.g. [189]). As the aim of the approach developed here is the detection of all petroleum hydrocarbons that can be extracted from a produced water sample, washing of the sorbent was neither desirable nor necessary. Instead, a step was introduced to remove residual water from the sorbent to avoid carryover into the elution sample. This was done by simply applying compressed air at controlled pressure to flush out any water that remained in the cartridge after loading was stopped. The final step is elution of the contaminants, application of approximately

3 × bed volume is typically recommended (100 mg bed weight $\approx$ 150 μ l volume). This is the minimum yielding best sensitivity, but the solvent volume can be increased depending on the specific application. To elute the hydrocarbons from the 900 mg bed weight cartridge, a volume of 10 ml was tested to give sufficient sensitivity while providing maximum recovery. Subsequent elution showed no additional release of hydrocarbons from the sorbent.

Table 3.1 below summarises the conditions tested and chosen for the solid-phase extraction procedure applied for the proof of concept of the SPE-NMR approach outlined in this chapter.

Table 3.1 Solid-phase extraction procedure for the isolation of crude oil contamination from an aqueous sample matrix and subsequent analysis with NMR spectroscopy.

	Conditioning	Loading	Washing	Elution
Compound(s)	Methanol & Water	Produced Water	Compressed Air	1 % CHCl ₃ in PCE
Volume [ml]	10 & 10	250	$\approx$ 10 - 15 bar	10

3.4 Alternative Analysis Methods

In order to validate the SPE-NMR results, alternative, well-established methods in the field of OiW analysis were chosen to provide independent measurements. Specifically, infrared (IR) spectroscopy, gas chromatography in combination with mass spectroscopy (GC-MS) and gas chromatography with flame ionization detector (GC-FID) were applied for validation purposes.

With respect to IR spectroscopy, the "ERACHECK PRO" from eralyticsTM GmbH (Vienna, Austria) was used. This is a compact, stand-alone infrared spectrometer with a quantum cascade laser (QCL), developed to measure total petroleum hydrocarbons (TPH) and oil and grease (OG) in water [193]. The analyzer has a measurement range from 0.5 to 2000 mg/L (oil in solvent) with absorption at wavelengths from 1370 to 1380 cm^{-1} . This corresponds to the CH₃ (methyl) bending vibration. Calibration of the instrument is necessary in order to yield a correlation between IR absorption and oil concentration. A calibration curve is usually established with the relevant crude oil (or a substance with similar composition) dissolved in the extraction solvent. In the case of the Eracheck, the extraction solvent is cyclohexane (or, alternatively, cyclopentane). Subsequently, liquid-liquid extraction of the produced water sample and IR-QCL measurement of the obtained extract is performed. Using the previously established calibration curve and the ratio of solvent to sample, the OiW concentration can be derived. The measurements of produced water with the Eracheck can be conducted in accordance with ASTM D7678-17 [194] giving either OG or TPH values.

Compared to conventional IR spectroscopy, which typically measures the stretch vibration frequencies of CH (aromatic), CH₂ (methylene) and CH₃, application of a QCL provides a much narrower spectral range. This offers the advantage of higher selectivity and the possibility to use environmentally compatible solvents. Nevertheless, the narrow spectral range can also prove

unfavourable as a constant ratio between the methyl groups and the aromatic as well as methylene groups has to be assumed. A change in composition will entail the necessity of a new calibration. Furthermore, components that do not contain methyl groups in their structure, e.g. benzene, will not be detected.

GC-MS and GC-FID were applied in this study for hexane and crude oil in water analysis, respectively. In gas chromatography, components of a test sample are evaporated and then distributed between a stationary and a mobile phase. The mobile phase is a stable, inert gas that carries the molecules through a column filled with either a solid adsorbent (gas-solid chromatography) or a liquid fixed onto an inert support (gas-liquid chromatography). The analytes are separated according to their retention times. The dominant factors that affect the retention times are the boiling point of the different species and their interactions with the stationary phase. The material of the latter can be chosen to provide minimum or weak interactions if the aim is separation on the basis of different boiling points. This is usually the case for the analysis of petroleum hydrocarbons. Gas chromatography needs to be combined with a suitable detector in order to detect and analyse the separated compounds as they leave the column.

The fundamental principle of detection with a mass spectrometer is based on the ionisation of neutral particles in the gas phase and acceleration of the resulting ions using an electric or magnetic field. Analysis of the ions according to their motion under the influence of that field follows. The output is a mass spectrum showing the ion signal versus the mass-to-charge ratio.

The GC-MS available for the proof of concept measurements uses a Quadrupole Mass Spectrometer. In this type of mass analyser, the ions pass through a mass filter that consists of four metal rods (see Figure 3.6a). A radio frequency voltage is applied to the rods to generate an oscillating electric field and only the ions that travel on stable trajectories will pass through and reach the detector. The other ions will collide with one of the metal rods to be neutralised. The trajectories are influenced by the mass of the ion as well as the strength of the electric field, hence by varying the r.f. voltage the oscillating electric field can be set to target specific ions. The detector records the charge of the ions as they hit its surface and establishes a spectrum with the number of detected ions as a function of their mass-to-charge ratio. In combination with gas chromatography, it is possible to separate and identify the compounds in an unknown sample. GC-MS is generally very sensitive to contamination (deflection of carrier gas or incomplete separation of the compounds), requires relatively pure samples and the spectra have to be interpreted carefully to avoid errors in the identification process (two different molecules might have a similar fragment pattern hitting the detector). In the case of good separation and limited number of compounds present, GC-MS may be used for quantification on the basis of total peak area of the target analyte. This of course, requires a calibration of the instrument with standard solutions of the target analyte prior to analysis.

Flame ionisation detection is another option for the analysis of compounds separated with gas chromatography. In this case, combustion and detection with a collector electrode form the basic

Figure 3.6 Schematic representation of detectors used for gas chromatography.

principle for analysis. The main components of a FID can be seen in Figure 3.6b. The analyte sample enters the FID through a heated connection to ensure the compounds remain in the gaseous phase after leaving the GC column. Just before the tip of the jet, the sample is mixed with hydrogen at a constant flow rate. As soon as the gas reaches the tip of the jet, it is lit by an electronic igniter to produce a hydrogen-air flame (excess air is supplied to ensure complete combustion). The organic compounds are cracked and form formylium ions via discharging electrons as they react with atomic oxygen. The electrons produced will be attracted by the positive biased jet while the formylium ions are collected by the negative biased collector electrodes (refer to Figure 3.6b). Thereby, a current is being induced which is the detected signal. The current is proportional to the ions produced in the flame and hence to the mass of carbon passing through the flame.

FIDs can exclusively detect organic substances and are well established in the petroleum industry for quantitative analysis of hydrocarbon mixtures. In theory, the detector response per carbon atom is the same for all organic compounds. The presence of heteroatoms causes the response factor to decrease, therefore effective carbon numbers should be used instead of a constant response factor. However, for the analysis of hydrocarbons where the heteroatom hydrogen is the same for all compounds, a response factor for a given detector can be determined (using a standard) and used to derive the concentration of unknown samples. Alternatively, a calibration can be established using standard solutions of the petroleum hydrocarbons in an organic solvent and correlating the peak area to the concentration.

As all hydrocarbons in a given analyte should evoke the same detector response, adequate separation using GC is essential prior to detection. For the analysis of a crude oil sample, a non-polar GC column, which provides negligible interaction between the hydrocarbons and the stationary phase, is typically used. The temperature of the column is ramped up slowly to achieve separation of the

hydrocarbons according to their boiling point and thus molecular weight. The separated compounds are then detected with the FID yielding a chromatogram such as the one shown below in Figure 3.7. Straight chain hydrocarbons show up as dominant peaks, whereas the branched hydrocarbons with the same carbon number will appear before the corresponding straight chain hydrocarbon (due to lower boiling points). If standards are available or retention times are known, the peaks can be readily allocated to hydrocarbon chain length.

Figure 3.7 Chromatogram of a light crude oil obtained with GC-FID analysis.

In the context of the work presented here, GC-FID is a valuable analysis method due to its linear range and high sensitivity to hydrocarbons. A GC-FID instrument from Agilent (Agilent 7890-A) was deployed for the validation measurements of the contaminated water samples. Furthermore, a Shimadzu GC-MS-QP2010 (GC-MS) was used for compound identification purposes and, to limited extent, for quantification of hexane in water.

3.5 Materials and Sample Preparation

Conditioning of the SPE sorbent material was performed using ACS grade methanol bought from Sigma-Aldrich (St.Louis, MO, United States) and deionised tap water.

Actual produced water samples were not available for the proof of concept measurements, therefore contaminated water was artificially prepared in the laboratory. CHROMASOLV[®] hexane (assay $\geq 97.5\%$) was used as a model compound to represent the aliphatic hydrocarbons in crude oil; this was obtained from Sigma-Aldrich (St.Louis MO, United States). Furthermore, a crude oil from a

local Western Australian reservoir was available for this study. Toluene was also purchased from Sigma-Aldrich (St.Louis MO, United States), HPLC assay 99.9%, to be used as a model compound for the aromatic hydrocarbons found in crude oil.

In terms of a solvent for SPE cartridge elution and subsequent NMR measurement, a mixture of 1% v/v chloroform (containing 100 - 200 ppm amylenes as stabilizer, assay $\geq 99.5\%$) in tetrachloroethylene (anhydrous, assay $\geq 99\%$), both purchased from Sigma-Aldrich (St.Louis, MO, United States), was used. This was selected as it is comparatively non-toxic and non-volatile, it provides a ^1H NMR spectral signal that is distinct from that of the aliphatic hydrocarbons and it is compatible with the SPE cartridges (as discussed in detail above).

Validation of the quantitative NMR measurements was conducted with standard solutions of hexane in the proposed solvent system. Initially, a stock solution of hexane in the solvent system was prepared that was subsequently diluted to cover a range of 100 to 1300 mg/L hexane in the solvent. This range corresponds to OiW concentrations of 4 to 52 mg/L taking into account 250 and 10 ml for the loading and elution volume during SPE, respectively.

Contaminated water samples were prepared by homogenising an excess amount of hexane, toluene or crude oil (relative to their respective solubility limits) in 2 L of deionised water for two minutes. The samples were then left overnight to equilibrate. During this process, an insoluble oil layer, originating from the excess amount of contaminant, formed on the surface. This layer was usually retained throughout the measurements to minimise contaminant loss via evaporation.

Cyclohexane (for HPLC, assay $\geq 99.9\%$) was obtained from Sigma-Aldrich (St.Louis MO, United States) for IR measurements. Calibration of the Eracheck was performed using hexane in cyclohexane and crude oil in cyclohexane over the range 10 to 1250 mg/L, respectively.

An Agilent HP-5MS UI column (30 m x 0.25 mm i.d.) with a nominal film thickness of 0.25 μm was available for GC analyses. This is a non-polar column with a stationary phase of (5%-phenyl)-methylpolysiloxane. The Shimadzu GC-MS-QP2010 was calibrated using hexane in propan-2-ol over the range 6 to 330 mg/L. To quantify the crude oil contamination in the samples, the Agilent 7890-A GC-FID with the Agilent HP-5MS UI column was used. Calibration was conducted with standard solutions of five different straight chain hydrocarbons (covering C_9 to C_{35}) in hexane in concentrations ranging from 12.5 to 100 mg/L. A detector response per carbon atom was calculated and subsequently used to determine the concentration of crude oil in the prepared samples.

3.6 Measurement Validation of Low-field qNMR

To validate the linearity of the quantitative NMR measurement over the conceivable range, samples of hexane in the 1 % CHCl_3 in PCE solvent were prepared gravimetrically and analysed with the 1 Tesla. Figure 3.8 shows the concentrations measured with NMR against the known gravimetric values.

Figure 3.8 Measured concentrations of hexane in the solvent determined with NMR versus the known gravimetric values. The lowest measurement of 100 mg/L hexane in the solvent corresponds to 4 mg/L in water as per the SPE conditions defined. The dashed line represents the line of equivalence ($y=x$).

Excellent linear correlation is evident between the quantitative NMR measurements and the gravimetric concentrations ($r^2 = 0.9985$). No deviations as a function of concentration are discernible.

To establish the repeatability of the qNMR measurement and data analysis, one sample was repeatedly analysed. The resulting standard deviation is less than 2 mg/L and compares well against the precision with which the samples can be prepared and stored. In Figure 3.8, the standard deviation is represented as error bars on the measurements, but these are not visible due to the small value.

3.7 SPE versus Conventional LLE

With the intention to confirm the ability of solid-phase extraction to achieve high recovery of hydrocarbons from an aqueous bulk phase, measurements were carried out using both SPE and the conventional LLE on contaminated water samples. Both hexane, as a model compound for aliphatic hydrocarbons in crude oil, and a light crude oil with negligible amounts of aromatics were used as contaminants to prepare two independent samples. The analysis was performed using the Eracheck (detailed above) in nine repeats. Additionally, the methodology applying SPE for pre-concentration and subsequent NMR analysis (SPE-NMR) on the hexane-in-water sample were carried out in triplicate. Based on the repetitive measurements, average concentrations of hexane- and oil-in-water and the standard deviations were derived and are summarised in Table 3.2.

Table 3.2 Concentration of hexane and crude oil in water with sample preparation using liquid-liquid and solid-phase extraction.

Sample	Concentration [mg/L]		
	LLE (IR)	SPE (IR)	SPE (NMR)
Hexane in water	14.74 ± 3.27	15.10 ± 2.09	15.4 ± 0.3
Crude oil in water	9.58 ± 4.00	8.18 ± 1.87	-

According to literature values, the solubility of hexane in water varies between 9.5 and 18.3 mg/L [195–197]. The measurements in Table 3.2 are consistent with this solubility range. Furthermore, excellent agreement was achieved between the LLE and SPE concentration methods as well as the IR and NMR analysis. With respect to the determined OiW concentrations, agreement is reasonable within the standard deviation across the repeated measurement. A larger standard deviation was derived using LLE for extraction and pre-concentration of the samples. This possibly reflects on the difficulty keeping the conditions consistent throughout the repeated extractions and ensuring that all contaminants are transferred to the solvent phase in the case of LLE application.

3.8 Hexane-in-water Analysis

In a next step, five independent samples of hexane dissolved in water were prepared. These were then analysed using the SPE-NMR methodology and GC-MS. The GC-MS was calibrated with standard solutions of hexane in isopropanol (see Section 3.5 above) and provides sufficient sensitivity to allow a direct measurement of the water samples. Figure 3.9 shows the concentration of hexane in the five independent samples as determined with SPE-NMR and GC-MS.

Good agreement is evident between the SPE-NMR and GC-MS results, the measurements track the variations in hexane concentration well. For this collection of measurements, the average concentrations of hexane in water were determined to be $c_{\text{hexane},\text{NMR}} = 11.1 \pm 3.6$ mg/L and $c_{\text{hexane},\text{GC-MS}} = 12.7 \pm 3.3$ mg/L; divergence of the two methods is well within the standard deviation. Again, this compares well against the literature values [195–197]. Variability of the results can be explained with different time delays between sample preparation and analysis as well as fluctuating experimental conditions, predominantly changes in temperature. This highlights the difficulty of OiW measurements in general. Preparing and storing samples of contaminated water is complex due to varying solubility limits as well as changes occurring over the storage time. Evaporation is a significant factor for OiW measurements as especially the lower molecular weight hydrocarbons have low boiling points resulting in relatively rapid loss from the liquid phase. Concentrations that are elevated when compared to the average or literature values, such as the ones from samples 2 and 5 in

Figure 3.9 Concentration of hexane in water from five independent samples measured with SPE-NMR and direct GC-MS analysis.

Figure 3.9, can originate from the hexane being dispersed or a hexane layer forming on the water surface during sample preparation. The latter essentially functions as a barrier to evaporation.

To extend this validation with alternative methods, additional samples of water contaminated with hexane were prepared and then analysed with the SPE-NMR methodology, GC-MS (direct) and IR absorption (combined with SPE). The measurements were performed in three repetitions — all applied methods — on two independent sample batches and it was attempted to keep the time lag between sample preparation and measurement consistent. The samples were prepared at a lower concentration to confirm the ability of SPE-NMR to quantify contaminants at < 10 mg/L in water. The individual SPE-NMR results for the two sample batches A and B are shown in Figure 3.10a, whereas Figure 3.10b details the average hexane concentrations in samples A and B as determined with SPE-NMR, GC-MS and IR.

The NMR measurements in Figure 3.10a average to $c_{\text{hexane},A} = 3.3 \pm 0.8$ mg/L and $c_{\text{hexane},B} = 3.4 \pm 0.6$ mg/L. Error bars represent the standard deviation across the triplicate repetition of the NMR measurement; these are consistent with those in Figure 3.8 and reflect the excellent repeatability of the NMR measurements. The low concentrations of the prepared sample batches are confirmed with the two alternative methods GC-MS and IR-QCL as displayed in Figure 3.10b. Agreement across the three applied methods is reasonably good, the NMR results sit in the middle of the other two methodologies. The slightly lower hexane concentrations determined with GC-MS are attributed to a significant longer time delay between sample preparation and measurement due to equipment access restrictions. Sample evaporation is more pronounced during extended storage times,

Figure 3.10 (a) Concentration of hexane in water determined through SPE-NMR analysis on two batches in three separate measurements. (b) Comparison of the hexane concentration in water of two samples A and B determined via the use of IR-QCL, GC-MS and NMR.

hence uniform experimental conditions are again shown to be critical to achieving high accuracy mg/L measurements and when comparing different methodologies. Nonetheless, the mutual agreement between SPE-NMR, GC-MS and IR-QCL evident in Figures 3.9 and 3.10 demonstrates the ability of the SPE-NMR methodology to perform reliably and consistently.

3.9 Oil-in-water Analysis

Following the hexane-in-water analyses, further investigations were conducted on water contaminated with an aliphatic crude oil obtained from a Western Australian reservoir. Three sample batches C, D and E were prepared. Of those, only sample batch C had an insoluble layer of oil on the water surface. The excess oil layer of batches D and E was removed prior to the experiments in order to provide lower concentrations. Again, three measurements of each batch were performed via IR-QCL, GC-FID and ¹H NMR, the results are summarised in Figure 3.11 below.

The frequency domain spectrum in Figure 3.11a illustrates the crude oil in the PCE-CHCl₃-solvent as produced during the SPE-NMR measurements with the 1 Tesla. The two peaks of the crude oil and the CHCl₃ reference are clearly distinct and their magnitudes are broadly comparable, thereby allowing quantitative analysis. Figure 3.11b shows the mg/L concentrations of crude oil in the sample batches as measured in three repetitions each with ¹H NMR analysis. Good consistency was achieved for each batch. The measurements average to give $c_{\text{crude oil},C} = 31.7 \pm 1.2$ mg/L, $c_{\text{crude oil},D} = 16.8 \pm 1.2$ mg/L and $c_{\text{crude oil},E} = 11.8 \pm 2.3$ mg/L, respectively. The larger concentration for batch C is a consequence of the insoluble oil layer on top of the water surface preventing contaminant loss as a consequence of evaporation. Given that no oil layer was left on samples D and E, they thus exhibit lower oil concentrations. This trend is reproduced with the other two analysis methods of GC-FID and IR-QCL as can be deduced from Figure 3.11c. Here, the

average concentrations for sample batches C, D and E determined with GC-FID, IR-QCL and SPE-NMR are shown.

Figure 3.11 (a) Spectrum of crude oil in the solvent system (PCE + CHCl₃) after SPE. 1 - resonance of CHCl₃. 2 - resonance of crude oil. (b) Concentration of crude oil in water determined through SPE-NMR analysis on three independent batches in three separate measurements. (c) Comparison of the crude oil concentration in water of samples C, D and E determined via the use of IR-QCL, GC-MS and NMR. Error bars represent the standard deviation from repetitive measurements.

Agreement across the three methods is good with the standard deviation $\sigma_C = 3.7$ mg/L, $\sigma_D = 3.8$ mg/L and $\sigma_E = 6.3$ mg/L for sample C, D and E respectively. Deviations can arise from the measurement protocol itself as it was not always practicable to adhere to the exact same experimental conditions. Furthermore, it is required to integrate over wide range of boiling points during GC-FID analysis which might result in substantial variations between measurements. This is reflected in the significantly larger standard deviation of the GC-FID measurement for sample D (see Figure 3.11c).

With respect to IR-QCL analysis, extrapolation is required due to the instrument being only sensitive to the methyl bond. A change in composition can add to the measurement error and cause the results to vary. However, this cannot be avoided as the solubility of crude oil is different for the solvent, cyclohexane, and water; the oil components will not dissolve homogeneously in water. However, overall the agreement is good and the SPE-NMR methodology is shown to be applicable to OiW samples. Further testing was required to optimise the SPE procedure in terms of sorbent material and experimental conditions. This is detailed in the following section.

3.10 SPE Optimisation

The SPE protocol applied for the extraction of crude oil contamination from an aqueous bulk matrix provided adequate recovery during the proof of concept measurements and compared well against LLE. One sorbent material consisting of octadecyl bonded silica, carbon loading of 11 %, was used for the measurements described thus far in this chapter. However, further investigation across a broader range of sorbent materials to ascertain the most suitable for isolating petroleum hydrocarbons, both aliphatics and aromatics, from water. Optimisation of the SPE procedure is also required to ensure maximum recovery while minimising the experimental time.

As discussed above, chemically bonded silica are generally recommended for an aqueous sample matrix. Hydrophobic interactions (non-polar analyte and non-polar sorbent) that induce analyte retention are enhanced if the sample medium is aqueous [198]. The water molecules have a high affinity for each other (hydrogen bonding) excluding any non-polar molecules present and thus causing the latter to concatenate with van der Waals forces. Van der Waals forces are relatively weak and non specific, which is beneficial when targeting with a wider range of target analytes with different sizes and structures. Petroleum hydrocarbons consist predominantly of non-polar molecules, hence the silica should preferably be bonded with a non-polar moiety to achieve maximum retention. Selectivity increases with decreasing chain length for hydrocarbon bonded silica. Of the available reversed-phase SPE sorbents, octadecyl bonded silicas are the least selective. Therefore, besides exploring C18 sorbents with varying carbon loading and obtained from different manufacturers, octyl bonded silica was considered. With regard to aromatic hydrocarbons, that can also be present in produced water and, depending on functional groups, have a higher polarity than straight chain hydrocarbons, phenyl bonded silica presents a potential option. To extend the initial investigations beyond the non-polar reversed-phase sorbents, cyanopropyl bonded silica was looked at as well. This sorbent can be used for both reversed-phase and normal-phase SPE to isolate moderately polar compounds in aqueous phases or polar compounds in organic solutions.

Carbon based materials can essentially be deployed as reversed-phase, normal-phase and ion exchanger sorbents, a comprehensive review is provided in [199]. Given the applicability of

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graphitized carbons for both polar and non-polar compounds, they are also a viable option for the sample preparation in the context of this doctoral research.

With the intention to assess the general suitability of a range of sorbent materials for the extraction of aliphatic and aromatic hydrocarbons from water, sample packs of SPE cartridges were obtained from Sigma-Aldrich and PhaseSep Pty Ltd (previously Grace). Table 3.3 summarises the materials available for initial testing.

Table 3.3 SPE material available for initial testing to isolate aliphatic and aromatic hydrocarbon from water. All of the listed chemically bonded silicas are endcapped. C8 - octyl. C18 - octadecyl. Ph - phenyl. CN - cyanopropyl

Name	Manufacturer	Material	Carbon load [%]	Particle size [μm]	Bed weight [mg]
Prevail C18	PhaseSep Pty Ltd	C18 on Silica	11	50	900
High-Capacity C18		C18 on Silica	17	50	1000
DSC-8	Sigma-Aldrich	C8 on Silica	9	50	1000
DSC-18		C18 on Silica	18	45	1000
LC-Ph		Ph on Silica	5.5	45	1000
DSC-CN		CN on Silica	7	50	1000
ENVI-Carb		Carbon	-	120-400 mesh	1000

In order to eliminate some of the available materials and narrow down the selection according to extraction efficiency of aliphatic and aromatic hydrocarbons from water, two samples of contaminated water were prepared. Sample F consisted of hexane dissolved in deionised water, whereas for sample G, toluene was used as the contaminant. Hexane and toluene were chosen as model compounds to represent the aliphatic and aromatic hydrocarbon fractions in crude oil, respectively. Due to the decrease in water solubility of saturated hydrocarbons with increasing chain length, hexane was chosen as a representative for the aliphatic fraction of the water soluble part of a crude oil. Toluene belongs to the BTEX compounds that can be present in produced water and was therefore chosen as a model compound for the aromatic fraction.

The samples were measured with SPE-NMR using the cartridges listed in Table 3.3. The measurements of sample F, hexane-in-water, were conducted according to the SPE protocol outlined above for the proof of concept. For sample G, the procedure was modified in order to take the higher water solubility of toluene, 515 and 724 mg/L [200, 197, 201], into account. Therefore, the loading volume needs to be reduced to avoid breakthrough. Consequently, a loading volume of 50 ml was

applied for the SPE procedure with sample G (sample F was loaded as usual using 250 ml). The rest of the steps were consistent with previous measurements — conditioning with 10 ml of methanol, then 10 ml deionised water, compressed air at 10 - 15 bar to flush out residual water and elution with 10 ml of the 1 % CHCl_3 in PCE solvent. Following the sample preparation with SPE, NMR analysis was performed on the 1 Tesla as outlined above (see section 3.2). Note that for the toluene samples, the self-calibrating characteristic of the measurement is lost due to a peak overlap of the resonances of the CHCl_3 and the aromatic ring. Figure 3.12 shows a typical frequency domain spectrum of toluene in the solvent system after SPE has been performed.

Figure 3.12 Typical ^1H NMR spectrum of toluene in the CHCl_3 -PCE-solvent after SPE obtained with the 1 Tesla. 1 - resonances of CHCl_3 and the aromatic ring of toluene. 2 - resonance of the CH_3 -group of toluene.

It is obvious that chloroform cannot be used as the direct reference in the case of toluene as the target analyte. For the quantitative analysis discussed in this section, the ratio between the aromatic and the methyl-group resonance was used to derive the integral area of the CHCl_3 . This ratio remains constant in the presence of other compounds or peak overlap. Prior to conducting the measurements, the ratio r was established for toluene and was subsequently applied to determine the peak area of the reference compound:

$$A_{\text{CHCl}_3} = A_{\text{CH}} - \frac{A_{\text{CH}_3}}{r} \quad (3.4)$$

Herein, A_{CHCl_3} , A_{CH} and A_{CH_3} are the integral areas of the chloroform resonance, the combined peak of the CH-resonances and the resonance of the methyl-group of toluene.

Further to the SPE-NMR measurements of the two samples, GC-FID analysis was conducted to validate the recovery of the different cartridges.

Figure 3.13 Concentration of (a) hexane and (b) toluene in water determined through SPE-NMR analysis and GC-FID. Seven independent measurements were conducted with SPE-NMR using different sorbent materials to assess their suitability for the extraction of petroleum hydrocarbons from water.

Figure 3.13a shows relatively good agreement across the materials and with GC-FID analysis for the determination of hexane concentration in water. The DSC-18 cartridge provides a larger measurement that is outside the solubility range reported in literature. This can be attributed to some residual contamination in the sorbent from the manufacturing process that was not removed during conditioning. In Figure 3.13b, showing the toluene concentration in water, the discrepancy between the cartridges is more significant. The cyanopropyl and phenyl bonded silica have the lowest recovery for the extraction of toluene from water. The octadecyl and octyl bonded sorbents perform similarly and achieve results that agree well with GC-FID analysis. The ENVI-Carb cartridge shows a comparably low recovery for toluene, whereas recovery for hexane is in line with the other sorbent materials.

Based on the results regarding recovery of hexane and toluene from water shown in Figure 3.13 the Prevail C18, High Capacity C18, LC-Ph and ENVI-Carb cartridges were chosen for further testing. The latter two were selected despite their poor toluene recovery in the initial test to provide an alternative to the chemically bonded silicas and, according to the manufacturer, they should demonstrate good affinity for both (slightly) polar and non-polar organic compounds. No significant discrepancy is observed between C8 and C18 bonded silica; C18 is preferred here as it ought to have a larger retention capacity and lower selectivity due to being less hydrophobic than C8 [198].

More comprehensive experiments were conducted to test the selected sorbent materials with respect to retention capacity and potential for reutilisation. This was done to eliminate sorbent materials that are not suitable to be incorporated in an automated SPE-NMR apparatus. To begin with, toluene recovery of the phenyl bonded silica cartridges LC-Ph was compared against C18 sorbents. Two samples A and B of contaminated water were prepared as described in Section 3.5 to be measured with SPE-IR and SPE-NMR, respectively. For the SPE procedure, cartridges were conditioned with methanol and water, then loaded with 20 ml of the sample and flushed with

compressed air. Elution was performed with 10 ml of cyclohexane or the PCE-CHCl₃-solvent, the resulting samples were immediately measured. The IR-QCL was calibrated with standard solutions of toluene in cyclohexane prior to conducting the experiments. Analysis of the NMR spectra was conducted using Equation 3.4. The samples were measured repetitively using a fresh cartridge for each run. The obtained concentrations of toluene-in-water are shown in Figure 3.14 for sample A analysed with SPE-IR (Figure 3.14a) and sample B analysed with SPE-NMR (Figure 3.14b). Direct GC-MS of the samples was also carried out and the resulting average value is displayed as a dashed line in each graph.

Figure 3.14 Comparison of C18 and Ph bonded silica sorbents with respect to toluene recovery from water using (a) SPE-IR on sample A and (b) SPE-NMR on sample B. GC-MS results are also shown as the average value from direct measurement in three repetitions on each sample.

The C18 sorbent exhibits a consistently better performance than the LC-Ph sorbent yielding a toluene concentration that is in good agreement with the respective GC-MS average. The toluene-in-water concentrations of $c_{\text{toluene},A} = 441.4 \pm 15.0$ mg/L and $c_{\text{toluene},B} = 378.5 \pm 42.5$ mg/L are lower than what literature data of the water solubility of toluene suggests (515 - 724 mg/L). This can be attributed to differences in sample preparation and experimental conditions. Both with IR and NMR analysis, it is determined that the phenyl bonded silica does not have sufficient ability to recover toluene from water. Therefore, the LC-Ph cartridges from Sigma-Aldrich were eliminated from the test matrix and not subjected to further investigation.

As shown in Table 3.3 above, three C18 cartridges with varying carbon loading were available for testing from two manufacturers. The DSC-18 cartridge from Sigma-Aldrich is very similar to the High Capacity C18 cartridge from PhaseSep Pty Ltd. These two cartridges showed comparable performance throughout the tests. For reasons of clarity and comprehensibility, the DSC-18 cartridges are disregarded in the following and the focus lies on the remaining cartridges, namely Prevail C18, High Capacity C18 and ENVI-Carb.

To begin with, the flow rate for the loading and elution step in the SPE procedure was investigated to see how it affects contaminant recovery. It is desirable to use the highest flow rate possible in order to minimise the time needed for loading/eluting. Here, the upper limit of a suitable flow rate was 5 ml/min as specified by the manufacturer. Exceeding this limit causes the pressure drop to increase significantly and does not provide sufficient interaction between sample and sorbent. Therefore, flow rates greater than 5 ml/min were not probed further. One sample of crude oil dissolved in water was prepared, which was then measured repeatedly with SPE-IR using Prevail C18 and ENVI-Carb cartridges. To determine the optimum flow rate, values between 2 and 5 ml/min were varied in 1 ml/min increments. The obtained OiW concentrations are shown in Figure 3.15 as a function of flow rate.

Figure 3.15 Effect of flow rate variation on OiW concentration determined with SPE-IR. The flow rate was varied between 2 and 5 ml/min. Prevail C18 and ENVI-Carb SPE cartridges were used for the SPE procedure.

From Figure 3.15, it can be concluded that varying the flow rate between 2 and 5 ml/min does not have an impact on the crude oil recovery. The standard deviation across the repeated measurements is < 2 mg/L for both cartridge types. Therefore, the maximum recommended flow rate of 5 ml/min is considered the optimum flow rate for determination of OiW through SPE-NMR and SPE-IR.

A significant factor with respect to an automated SPE-NMR device is the reusability of the cartridges. This has to be considered in order to develop a system with a limited supply of SPE cartridges that can run for an extended time period without manual intervention. Preliminary measurements were conducted with the Prevail C18 and the ENVI-Carb cartridges on several independent samples of water contaminated with crude oil. These experiments were carried out applying the SPE protocol from the proof of concept measurements (250 ml load volume, 10 ml

elution volume). However, the same cartridge was reused several times and thus the conditioning step was only performed once prior to the first SPE run. For the subsequent solid-phase extractions, any residual solvent was pushed out of the sorbent using compressed air and the cartridge then loaded again with the sample. Three independent sample batches A, B and C were prepared. These were then analysed with SPE-NMR in three repetitions with both cartridges on each sample. Figure 3.16 summarises the measurements on each sample batch with the two cartridges.

Figure 3.16 Oil concentration in water of three independent samples A, B and C as determined with SPE-NMR reusing one Prevail C18 and one ENVI-Carb. In between reuses, the cartridges were not conditioned.

Note that for measurement C1, a fresh ENVI-Carb cartridge was used due to significant degradation of the first cartridge. During the five uses of ENVI-Carb cartridge #1, some of the carbon sorbent penetrated through the bottom frit and was consequently lost. As is conveyed when comparing the ENVI-Carb measurements versus those with Prevail C18, the retention capacity of the carbon sorbent decreased with increasing number of reuses and is not able to capture the oil concentration accurately any more. Consequently, the carbon was rejected as a potential sorbent for the automated SPE-NMR device and not considered for later experiments. All subsequent measurements were carried out with the cartridges purchased from PhaseSep Pty Ltd (High Capacity C18 and Prevail C18) with the intention to optimise the SPE procedure regarding conditioning, flow rate as well as loading and elution volumes.

Loading the sorbent with the sample is the most time-consuming step in the SPE procedure due to a maximum possible flow rate of 5 ml/min and the comparatively large volume involved. For the measurements of hexane or crude oil in water shown previously, a loading volume of 250 ml was deployed, hence requiring 50 min for the loading step alone. In order to reduce the overall time for the

SPE procedure, the minimum loading volume that is representative of the sample, achieves sufficient pre-concentration for the subsequent analysis and is large enough to compensate for any fluctuations of contaminant concentration within the sample was explored. It was assumed that a minimum value exists above which an increase in the loading volume does not yield more accurate results.

To establish the minimum load volume required for reliable OiW measurements, SPE-NMR and SPE-IR measurements with varying load volumes have been carried out on two independent contaminated water samples (sample A contaminated with hexane, sample B with crude oil). A fresh (conditioned) cartridge was used for each run and the loading volume was varied between 50 and 350 ml in 50 ml increments. The air flush and solvent elution were consistent with the SPE protocol thus far applied. Figure 3.17 shows the concentration of hexane and crude oil in samples A and B, respectively, plotted versus the applied loading volume.

Figure 3.17 Optimising the loading volume of the SPE procedure. (a) Hexane concentration in water determined with SPE-NMR measurements with the loading volume varied from 50 to 300 ml. (b) Crude oil concentration in water determined with SPE-IR measurements with the loading volume varied from 50 to 350 ml. The dashed line represents in (a) $c_{avg,hexane} = 12.2 \pm 2.5$ mg/L and in (b) $c_{avg,crude\ oil} = 5.9 \pm 0.3$ mg/L, the average concentration derived from the measurements with 150 to 300 ml and 150 to 350 ml load volume, respectively.

It can be seen that the concentration initially decreases with increasing load volume and then plateaus. This is more evident in Figure 3.17b, where an average of $c_{avg,crude\ oil} = 5.9 \pm 0.3$ mg/L is derived for the last five measurements demonstrating good consistency for load volumes greater than 150 ml. For sample A (Figure 3.17a), analysed with NMR, the hexane concentration averages to $c_{avg,hexane} = 12.5 \pm 2.5$ mg/L yielding a slightly larger standard deviation with a less prominent plateau. It was concluded that for samples with a contaminant concentration down to 5 mg/L, a loading volume of 150 ml is sufficient to provide accurate measurements. As a result, the time needed for the loading step is reduced to 30 min. Note that in the case of a very low contaminant concentration, < 5 mg/L, the loading volume has to be reassessed and adjusted to achieve adequate pre-concentration.

Furthermore, the optimum solvent volume for the elution step in the SPE procedure has to be established. The smallest possible volume should be used that achieves the highest recovery of the target analyte from the sorbent material. The SPE protocol established for the proof of concept applies 10 ml of elution solvent, which has been used for the measurements shown thus far in this chapter and was shown to yield accurate results. With the intention to determine if the solvent volume needs to be increased for the elution of hydrocarbons from C18 cartridges, SPE-NMR measurements were carried out with stepwise elution.

A sample of crude oil dissolved at a relatively high concentration, i.e. > 30 mg/L, in water was prepared. The SPE procedure was carried out using the previously deployed protocol: 250 ml loading volume, compressed air flush and then, in a first elution, 10 ml of the CHCl_3 -PCE-solvent. Three additional elutions were then performed with 2 ml each to check if more crude oil can be recovered from the sorbent. The volumes and determined concentrations were summed to establish the recovery for elution volumes of 10, 12, 14 and 16 ml. This measurement was repeated multiple times, both using SPE-NMR and SPE-IR measurements. An excerpt of the results is shown in Figure 3.18 where the concentration of crude oil in water as determined with SPE-NMR with three independent cartridges is plotted versus the applied elution volume.

Figure 3.18 Elution volume optimisation for the SPE-NMR procedure to determine the minimum amount of solvent required for maximum contaminant recovery. Crude oil concentration as a function of elution volume is shown for three measurements performed with Prevail C18 SPE cartridges.

It can be seen in Figure 3.18 that increasing the elution volume beyond 10 ml does not present higher hydrocarbon recoveries. The additional elutions yielded clean NMR spectra with no visible crude oil peak. Consequently, a solvent volume of 10 ml was considered appropriate for the elution of crude oil contaminants from SPE cartridges with a bed weight of 900 to 1000 mg.

Following the optimisation of the SPE procedure to minimise time and solvent used, further measurements were conducted with the two selected sorbent materials, Prevail C18 and High Capacity C18. Here, the objective was to investigate if omitting the conditioning step negatively affects the extraction performance of the cartridges. For this purpose, the SPE procedure was performed with two cartridges of each type at the same conditions and on the same sample. One cartridge of each type was directly loaded without pre-conditioning whereas the other was conditioned with methanol and deionised water and then loaded with the sample. The comparison of conditioned versus non-conditioned cartridges is shown in Figure 3.19a for the Prevail C18 and in Figure 3.19b for the High Capacity C18 cartridges on three independent water samples contaminated with crude oil.

Figure 3.19 Effect of omitting conditioning on the performance of (a) Prevail C18 and (b) High Capacity C18 cartridges on the recovery of crude oil from water. The samples of water contaminated with crude oil were prepared independently at varying concentrations, no correlation between the samples in (a) and (b) exists.

Omitting the conditioning step for the deployment of Prevail C18 cartridges has a minimal effect on the determination of OiW concentration and no trend can be observed. The measurements agree well with each other with a slightly larger discrepancy for higher crude oil concentrations. The High Capacity C18 cartridges on the other hand deviate more significantly between conditioned and non-conditioned cartridges. In view of automating the SPE procedure with minimised complexity, hence with as little equipment and (solvent) supplies as feasible, a decision was made to proceed with the Prevail C18 cartridges/sorbent material.

The optimisation measurements regarding the SPE procedure carried out using both IR-QCL and NMR analysis have led to the selection of the Prevail C18 sorbent for the extraction of crude oil from aqueous samples. This sorbent performed best with regards to consistent recovery efficiencies and it does not need conditioning prior to the SPE procedure. Optimal SPE conditions were established and are summarised in Table 3.4 below.

Table 3.4 Optimised solid-phase extraction material and procedure for the isolation of crude oil contamination from an aqueous sample matrix and subsequent analysis with NMR spectroscopy.

Sorbent	Bed weight [mg]	Loading volume [ml]	Elution volume [ml]	Flow rate [ml/min]
Prevail C18	900	150	10	5

3.11 Conclusion

The methodology of using solid-phase extraction in combination with quantitative NMR has been developed for the determination of oil-in-water at the ppm level. Initially, it was demonstrated that the qNMR analysis deploying a low-field spectrometer exhibits excellent linearity over the conceivable concentration range. These measurements were performed using standard solutions of hexane in the selected solvent system consisting of 1% CHCl_3 in PCE. Subsequently, the SPE procedure was implemented in a semi-automated procedure in the laboratory with commercially available SPE cartridges and a simple peristaltic pump to apply the loading and elution volumes. Through the measurement of various independent water samples that were contaminated with hexane and crude oil, respectively, the SPE-NMR approach was trialled. Validation of the developed methodology was carried out using the alternative methods IR-QCL, GC-MS and GC-FID to provide independent measurements of the same samples. The concentration of hexane in water determined with SPE-NMR has proven to compare well against the alternative measurements as well as literature values. Furthermore, it was demonstrated that concentrations <5 mg/L can be captured accurately. With respect to assessing crude oil dissolved in water, SPE-NMR compares favourably with IR-QCL and GC-FID and is capable of tracking varying sample concentrations. The standard deviation across three repeated measurements were 2 mg/L and lower showing the ability of SPE-NMR to provide consistent results.

The SPE procedure was subjected to optimisation in order to achieve maximum recovery and minimal experimental time. Seven sorbent materials obtained from two manufacturers were investigated regarding recovery efficiency of hexane, toluene and crude oil from water. In addition to highest recovery, the parameters of reusability as well as complexity of the SPE procedure, specifically the feasibility of omitting the conditioning step, were considered for sorbent selection. The Prevail C18 sorbent demonstrated best performance overall. It is able to retain both aromatic and aliphatic hydrocarbons from water, can be reused for multiple times on water contaminated with crude oil without signs of degradation or performance loss and does not need conditioning. Apart from sorbent selection, the operational parameters of the SPE procedure — flow rate, loading volume and elution volume — were optimised with the overall objective to minimise the experimental time. Specifically, the volumes were minimised while retaining recovery efficiency and the flow rate maximised. A maximum flow rate of 5 ml/min was established for both loading and eluting. The

optimal loading volume was determined at 150 ml yielding reliable measurements while not overloading the sorbent and causing breakthrough (verified with GC-FID). It was shown that smaller volumes were not representative of the whole sample. It must be noted that the loading volume needs to be checked and potentially adjusted in the case of very low or high contaminant concentration in the sample. Eluting with 10 ml of solvent removes the maximum of retained contaminants in the sorbent; this has been confirmed with NMR, IR-QCL and GC-FID. The total experimental time required for SPE-NMR measurements in a half-automated approach applying the optimised methodology is 50 min.

Overall, the SPE-NMR methodology provides robust measurements of oil-in-water at concentration between 2 and 100 mg/L. The SPE procedure was optimised and the best performing sorbent material selected. Furthermore, the approach has the potential to be automated as both the SPE procedure itself and the NMR measurement can be carried out without manual intervention. On the basis of the successful proof of concept demonstrated in this chapter, the SPE-NMR methodology has been developed into a fully automated prototype. The design, development and testing of the prototype is the subject of Chapters 5 and 6. Extension of the SPE-NMR approach to include the simultaneous and self-calibrated quantification of aromatic and aliphatic hydrocarbons in the same sample will be discussed in Chapter 4.

Chapter 4

Quantification of Aromatic and Aliphatic Hydrocarbons in Water

The simultaneous quantification of the aromatic and aliphatic contribution to the total oil content in produced water using qNMR analysis forms the subject of this chapter. Section 4.1 provides the background to the requirement of a more detailed analysis of produced water and the current state-of-art in this context. This is followed by a description of the proposed methodology in the form of an extension of the previously developed and verified SPE-NMR approach (Section 4.2). The experimental details of the measurements are summarised in Section 4.3 and the results obtained presented and discussed in Section 4.4. The chapter finishes with a conclusion and outlook regarding the developed methodology (Section 4.5).

4.1 Background

Regulations regarding the discharge limit of produced water are governed by the total oil content in the discharge stream. Offshore installation can be required to demonstrate BAT with respect to water treatment (e.g. in the US) or have to show that environmental impacts are reduced to as low as reasonably practicable (ALARP), e.g. in Australia [30]. However, toxicity of the dissolved and/or dispersed organic compounds and effects on the aquatic life is increasingly being considered in recent years. Norway, which can be regarded as one of the pioneers in the oil and gas industry constantly advancing new technologies and attempting to find a balance between oil exploration and environmental stewardship, has started a zero harmful discharge initiative in the late 1990s. The target are naturally occurring organic substances, including aromatic hydrocarbons, as well as chemical additives that are hazardous to the marine environment. The zero harmful discharge initiative led to reduced discharge of environmentally harmful substances [202] and to a decline in average oil concentration in discharge water to 10 - 15 mg/L [203] (which satisfies the monthly

average limit at 30 mg/L set by the OSPAR Convention). It is expected that the Norwegian regulator will set a stricter limit in the near future [204]. Generally, a shift towards assessing the toxicity of the discharged substances, rather than simply specifying the total oil content, is anticipated as climate change considerations become more influential. In this respect, OSPAR has adopted measures to regulate the amount of hazardous substances discharged to the sea together with produced water. In 2012, OSPAR Recommendation 2012/5 was enacted [205] implementing risk-based approach towards the management of produced water that requires characterisation of the environmental risk of a produced water discharge.

Water solubility and persistence are critical with respect to toxicity of an organic compound to aquatic life [206, 207]. Typical aromatic hydrocarbons present in produced water are the BTEX compounds (benzene, toluene, ethylbenzene and xylene), phenols and polycyclic aromatic hydrocarbons — these have comparatively higher water solubilities than the aliphatic contaminants [196, 208, 201, 209–211, 200, 212]. Decreasing length of the hydrocarbon chain generally indicates larger water solubility but also higher volatility, hence loss from the aqueous phase via evaporation occurs more readily. Various studies have investigated the impact of hydrocarbons on the aquatic environment concluding that aliphatic hydrocarbons impose little impact to the marine environment [213]. Aromatic hydrocarbons, especially BTEX, are the most abundant hydrocarbons dissolved in the produced water stream and can be highly toxic [214]. Due to their typically low boiling points and thus high volatility, aromatic compounds are rapidly lost from surface water discharges [215]. However, this is not the case for discharges at appreciable depths, such as when considering subsea separation facilities where the produced water will supposedly be released at the wellhead. Here, specifically polycyclic aromatic hydrocarbons (PAH) are of significant environmental concern due to both their persistence and toxicity to aquatic life [216]. Aquatic hazards including both short- and long-term effects introduced by the presence of aromatic hydrocarbons should not be neglected [206, 217, 218] even at low concentrations [219].

The increasing awareness regarding the ecological footprint affects the functional requirements demanded from OiW sensors. It is of interest to quantitatively separate the aromatic and aliphatic contributions to the total oil contamination. However, the commercially available options of on-line or in-field devices are only able to provide total OG or TPH measurements and either dispersed (for example with imaging) or dissolved (UV fluorescence) oil is determined. A more detailed assessment needs more comprehensive laboratory methods, such as GC-FID. In this context, extension of the previously established SPE-NMR methodology is explored to accurately determine the aromatic and aliphatic contributions to total oil contamination in produced water at the ppm level.

4.2 Methodology

This section outlines the SPE-NMR approach to quantitatively measure aromatic and aliphatic hydrocarbons in the same sample and briefly describes how the measurement uncertainty is assessed.

4.2.1 Advanced SPE-NMR

The SPE-NMR approach described and validated in Chapter 3 of this thesis uses a solvent system of 1 % v/v CHCl_3 in PCE as the elution solvent for the SPE procedure and to provide the internal ^1H NMR reference in the subsequent analysis. This renders the qNMR measurement effectively self-calibrating giving it a significant advantage over most other available OiW monitors that need frequent calibration. Application of CHCl_3 as the single reference performs adequately given a crude oil or condensate that consists predominantly of aliphatic hydrocarbons. These resonate at a chemical shift of $\delta = 0.9 - 1.4$ ppm with sufficient separation from the CHCl_3 resonance at $\delta = 7.26$ ppm (refer back to Figure 3.3). Aromatic rings exhibit ^1H NMR resonance frequencies that are similar to the CHCl_3 frequency generated by the single proton bonds of their structure. Consequently, CHCl_3 cannot be deployed as a single, internal reference to yield a self-calibrating measurement when aromatics are present.

Here, a new approach is suggested that extends the SPE-NMR methodology for the quantification of total oil concentration to include the determination of the aromatic and aliphatic contribution. The extended approach, hereafter referred to as Advanced SPE-NMR, is based on the application of two solvent mixtures, that both contain two reference compounds at defined concentrations, and a twofold NMR measurement. For the selection of suitable reference compounds, the target analyte(s) and their respective chemical shifts have to be considered. Furthermore, the reference compounds need to be soluble in the PCE solvent and should present resonances significantly separate in ^1H NMR.

To enable the differentiation of aromatic and aliphatic hydrocarbons with approximate chemical shifts of $\delta = 7 - 8$ and $\delta = 0.9 - 1.4$ ppm, respectively, the (previously used) reference compound CHCl_3 and hexamethyldisiloxane (HMDSO) with $\delta = 0.09$ ppm [185] were chosen. Two solvent mixtures using PCE as the base solvent were prepared to each contain both reference compounds, but at different ratios. In the work presented here, concentrations of 0.175% HMDSO and 1% CHCl_3 v/v in PCE for solvent mixture 1 and 0.1% HMDSO and 1.5% CHCl_3 v/v in PCE for mixture 2 were used initially. These starting values were later optimised in terms of their collective sensitivity to quantify the aliphatic and aromatic content (discussed in Section 4.4.3 below). ^1H NMR spectra of the two solvent mixtures 1 and 2 obtained with the Spinsolve can be seen in Figures 4.1a and 4.1b, respectively.

Figure 4.1 Sample ^1H NMR spectra of the chosen solvent mixtures of (a) 0.175% HMDSO and 1% CHCl_3 v/v in PCE (mixture 1) and (b) 0.1% HMDSO and 1.5% CHCl_3 v/v in PCE (mixture 2). The rectangles mark the integral areas, where the ratios a_1/b_1 and a_2/b_2 are determined as detailed in Equation 4.1 in the text.

Figure 4.1 demonstrates that the reference compounds produce single, sharp resonances sufficiently separate (308 Hz) at a magnetic field strength of 1 Tesla. In order to quantify the aliphatic and aromatic content in a sample, the integral areas around the reference peaks have to be determined for the two solvent mixtures. The rectangles in Figures 4.1a and 4.1b highlight the chemical shift ranges established for integration. These are consistent for both mixtures. The chemical shift ranges were chosen in view of the application to field samples of produced water, where peak broadening is expected due to the complex composition of the samples and fluctuating surrounding conditions. The following ratios are derived from the obtained spectra in Figure 4.1:

$$r_1 = \frac{a_1}{b_1} \text{ \& } r_2 = \frac{a_2}{b_2} \quad (4.1)$$

Herein, a refers to the integral area around the HMDSO peak and b to the one around CHCl_3 . The indices 1 and 2 are indicative of the two solvent mixtures 1 and 2, respectively. Peak area integration is performed for a from -0.5 to 3.25 ppm and for b from 6 to 8.5 ppm. The ratios r_1 and r_2 are constants for the original ("pure") mixtures, determined to be $r_1 = 1.4$ and $r_2 = 0.6$ for the spectra presented in Figure 4.1. The values vary slightly for different solvent batches, hence they were measured for freshly prepared mixtures and regular checks were performed to confirm consistency.

After introducing contaminants to the solvent mixtures, here decane and toluene were used as model compounds to represent aliphatic and aromatic hydrocarbons, respectively, ^1H NMR spectra were measured. Sample spectra of the two solvent mixtures spiked with decane at 730 mg/L and toluene at 864 mg/L are shown in Figure 4.2. The total contaminant concentration of 1594 mg/L in the solvent is typical of what can be expected when using the Advanced SPE-NMR to measure the contamination of a produced water sample.

Figure 4.2 Sample ^1H spectra of the contaminants toluene and decane in the solvent mixtures (a) 1 and (b) 2. The rectangles mark the integral areas, c_1 and c_2 include the HMDSO as well as the methyl and methylene (generated by the toluene and the decane, respectively) resonances, whereas d_1 and d_2 contain the CHCl_3 along with the aromatic ring resonance.

In Figures 4.2a and 4.2b, the contaminant peaks appear close to the HMDSO resonance and as a shoulder peak on the CHCl_3 resonance. It is evident that the HMDSO resonance is distinguishable and can be deployed as a direct, internal reference for quantification. However, Figure 4.2 is obtained from a benchtop NMR spectrometer used under well controlled conditions, where the temperature is stable and the magnet recently shimmed. Furthermore, the linewidth of the hydrocarbon species will inevitably broaden when the model compounds decane and toluene are replaced by a crude oil due to increased variety of the compounds contributing to the resonances. In order to provide a methodology that is more robust and does not require clean peak separation, the integral areas are defined to include both the reference and contaminant compounds. As indicated in Figure 4.2a and 4.2b, the integral areas c and d are defined with identical ranges to a and b , respectively. Equations 4.2 shows c to be the sum of the HMDSO and the aliphatic resonances whereas d combines the CHCl_3 and aromatic resonances.

$$\begin{aligned} c_1 &= a_1^* + x \text{ \& } c_2 = a_2^* + x \\ d_1 &= b_1^* + y \text{ \& } d_2 = b_2^* + y \end{aligned} \quad (4.2)$$

Herein, x represents the integral peak area of the methyl and methylene resonances (aliphatic) and y represents the aromatic peak area. It is assumed that the two samples contain the same amount of contaminants. The asterisk distinguishes the actual values for the integral peak areas of the reference compounds in the samples from those in the original solvent mixtures measured previously ($a \neq a^*$ & $b \neq b^*$). It must be noted that it is essential to provide two independent pieces of information in order to derive the two unknowns, the aliphatic and aromatic content. Therefore, the twofold measurement approach to provide two independent ^1H NMR spectra is required.

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Subsequently, Equations 4.2 and 4.1 can be combined and rearranged to solve for the actual peak area of the CHCl_3 in mixture 2 (Figure 4.2b), b_2^* :

$$b_2^* = \frac{c_2 - d_2 r_1 + d_1 r_1 - c_1}{r_2 - r_1} \quad (4.3)$$

Calculation of b_2^* can be performed with c_1 , c_2 , d_1 and d_2 as well the ratios of the reference compounds in the original solvent mixtures, r_1 and r_2 . With b_2^* quantified, the peak area of the aromatic resonance (y) can be derived via subtraction of b_2^* from d_2 (refer to Equations 4.2). In addition, knowledge of b_2^* also enables derivation of a_2^* given the constant ratio r_2 (Equations 4.1). This subsequently allows calculation of the integral of the aliphatic hydrocarbon contaminant resonances x and thus the individual peak areas relating to HMDSO, CHCl_3 , aliphatics and aromatics are deduced. The relevant equations are summarised as follows:

$$\begin{aligned} y &= d_2 - b_2^* \\ b_1^* &= d_1 - y \\ a_2^* &= r_2 b_2^* \\ a_1^* &= r_1 b_1^* \\ x &= c_2 - r_1 b_2^* \end{aligned} \quad (4.4)$$

Given Equation 2.22 (detailed in Chapter 2), the concentrations of the target analytes decane and toluene can be determined. With respect to Figure 4.2, the amounts of decane and toluene in the samples were thus measured to be 551 and 661 mg/L, respectively, giving a combined concentration of 1212 mg/L. These values agree reasonably well with the expected gravimetric concentrations of 525 mg/L for decane and 622 mg/L for toluene, presenting a total oil concentration of 1147 mg/L. The deviation between measured and known values for the total oil concentration as well as the individual aromatic and aliphatic content is less than 6 %.

In the above calculations, the methyl component of the toluene was reassigned to the aromatic content based on prior knowledge of the exact composition. In practice, where produced water samples with an unknown composition of the contaminants are measured, such reassignment cannot be readily performed. In this case, a prominent aromatic component of the relevant crude oil can be assumed and the correction applied accordingly.

Due to the complexity of the sample preparation and measurement, error analysis to determine the uncertainty associated with the NMR measurement and gravimetric sample formulation is performed and detailed below in Section 4.2.2 and in Appendix A.

4.2.2 Measurement Uncertainty

(Random) error or uncertainty can occur both with respect to the preparation of validation samples as well as with respect to the execution and analysis of the required NMR spectra. Given the ppm concentration requirements, the former can be quite acute. However, both need to be analysed in order to compare and evaluate the measurement uncertainty versus the sample preparation uncertainty. The resultant combined measurement uncertainty u_c , associated with the quantification of the aliphatic and aromatic (decane and toluene) content using the Advanced SPE-NMR approach as well as the uncertainty related to sample preparation are detailed in Appendix A.

The combined measurement uncertainty u_c is subsequently transformed into an expanded uncertainty, U , defined as the interval around the measurement result that corresponds to a % confidence interval [220] via:

$$U = k u_c \quad (4.5)$$

95 % is a common choice for the confidence interval, in which case $k = 2$. Referring back to the spectra shown in Figure 4.2, the uncertainty associated with qNMR analysis using the Advanced SPE-NMR approach was determined to be less than 5 %. This compares reasonably well against the accuracy with which the samples can be prepared; this is estimated to be 2 % for the samples displayed in Figure 4.2.

4.3 Experimental

In the following, the materials used for the experiments, preparation of the samples, information regarding the instrumentation and the experimental procedure followed are detailed.

4.3.1 Materials

As already described with respect to Figure 4.2, decane (anhydrous, assay $\geq 99\%$) and CHROMASOLV[®] Plus toluene (for HPLC, assay $\geq 99.9\%$) were used as model compounds for aromatic and aliphatic contaminants in order to validate the proposed methodology. In regard to the solvent mixtures applied, PCE (anhydrous, assay $\geq 99\%$) constitutes the base solvent with no ^1H NMR signal. CHCl_3 (with 100 - 200 ppm amylenes as stabilizer, assay $\geq 99.5\%$) and HMDSO (NMR grade, $\geq 99.5\%$) were used as reference additions to the solvent. All chemicals were obtained from Sigma-Aldrich (Sigma-Aldrich, St.Louis MO, United States). A light crude oil containing mainly aliphatic hydrocarbons was retrieved from a local Western Australian reservoir. Commercially available SPE cartridges were used, as was the case during the proof of concept measurements presented in the previous chapter. These contained silica based, octadecyl bonded sorbent material

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with a carbon load of 11 % and an average particle size of 50 μm . The cartridges were obtained from PhaseSep Pty Ltd (PhaseSep Pty Ltd, the Pines VIC, Australia).

4.3.2 Sample Preparation

As explained above, two solvent mixtures were made up to contain 1 % v/v CHCl_3 and 0.175 % HMDSO for mixture 1, and 1.5 % v/v CHCl_3 and 0.1 % HMDSO in PCE for mixture 2. Decane and toluene were then added to the two solvent mixtures such that the nine samples detailed in Table 4.1 could be prepared. This was done via dilution of an initial stock solution at high concentration (detailed as *stock* in Table 4.1) to the other required sample concentrations. Table 4.1 shows the individual compositions of the nine samples, selected to be consistent with the conceivable concentration range required to be measured using the Advanced SPE-NMR procedure. A range of 191 to 2869 mg/L of contaminant in solvent was chosen which corresponds to 13 to 191 mg/L oil-in-water when applying the SPE procedure as established previously (a loading volume of 150 ml contaminated water and elution with 10 ml of solvent).

Table 4.1 Concentration of decane and toluene in the model mixtures 1 and 2 for measurement validation of the Advanced SPE-NMR methodology. One stock solution of the contaminants in each solvent system was made up, the measured samples were then prepared by combining a portion of the stock solution with the respective pure solvent mixture.

Sample	Decane [mg/L]	Toluene [mg/L]	Total oil [mg/L]	Corresponding oil-in-water [mg/L]
<i>stock</i>	4380	5182	9562	637
# 1	88	104	191	13
# 2	131	155	287	19
# 3	219	259	478	32
# 4	350	415	765	51
# 5	526	622	1147	76
# 6	657	777	1434	96
# 7	876	1036	1912	127
# 8	1095	1295	2390	159
# 9	1314	1555	2869	191

Subsequent to this measurement validation, two test water samples (hereafter referred to as samples A and B) contaminated with crude oil and toluene were prepared for compositional analysis via the Advanced SPE-NMR technique. This was done by homogenising 0.5 ml and 1 ml of crude oil as well as 80 μL and 200 μL of toluene in 2 L of water, respectively (hence forming sample A and B). In the case of toluene, the solubility in water is known to vary between 500 - 600 mg/L [200, 197, 196].

Based on previous measurements on a similar source of crude oil, the crude oil water solubility is approximately between 5 and 30 mg L. This variability in solubility reflects both compositional variations as well as differences in temperature and possibly background water chemistry. In any case, the objective was to produce two water samples (A and B) of different mg/L oil contaminant composition. Both samples were equilibrated overnight and, if present, the excess oil layer was skimmed off the water surface. The Advanced SPE-NMR analysis was then applied alongside independent validation measurements using SPE-IR-QCL and SPE-GC (as detailed previously in Section 3.4) to determine the total oil concentration as well as the contributions of aromatic and aliphatic content.

4.3.3 Instrumentation

The ^1H NMR spectra were obtained with the Spinsolve benchtop spectrometer built by Magritek Ltd., New Zealand (hereafter referred to as the Spinsolve) shown in Figure 3.1b, Chapter 3. All NMR measurements were performed at a magnet temperature of 28°C using a standard, simple r.f. pulse and collect sequence. A 90° r.f. pulse with a duration of $7\ \mu\text{s}$ was deployed and measurements were averaged over 8 scans with a repetition time (T_R) of 15 s, thus giving a total acquisition time of 2 min. These parameters were kept constant throughout all measurements. The longest potential longitudinal relaxation times present were provided by the reference compound CHCl_3 in the PCE solvent (determined to be 2.8 s) and the resonance of the aromatic ring of the toluene at 3 s. Therefore, with a T_R of 15 s, the commonly applied criteria for quantitative spectroscopy of $T_R \geq 5T_1$ is met.

To validate the NMR results from the contaminated water samples, gas chromatography in combination with flame ionization detector (GC-FID) was used. GC-FID is the applicable reference method for determination of dispersed OiW in Australia as defined by the OSPAR convention [28]. For the measurements presented here, an alternative sample preparation (namely reversed-phase SPE) in combination with a comparable GC-FID analysis methodology was applied. The GC-FID instrument available was a Thermo Scientific™ Trace™ 1300 GC equipped with a flame ionization detector and autosampler. The capillary column was a TraceGold TG-5MS column (30 m x 0.25 mm i.d.) with a nominal film thickness of $0.25\ \mu\text{m}$. Similarly to the measurements presented in the previous chapter (Chapter 3), calibration was conducted with standard solutions of toluene in cyclohexane as well as crude oil in cyclohexane. The solutions covered range of 50 to 500 mg / L contaminant in solvent. For crude oil analysis, integration was performed from C9 onwards and plotted versus the gravimetric concentration to establish a calibration curve. Hydrocarbon standards were measured to provide the retention times of the straight chain hydrocarbons. With appropriate calibration and knowledge of relevant retention times, chromatograms from GC-FID measurements can be used to quantify the individual compounds in the system. This is exploited here to extract the toluene concentration in the contaminated water samples by using its specific retention time as determined through prior calibration measurements. Note however that individual determination is not

longer readily possible when a mixture of various aromatic and aliphatic contaminants as retention times and thus peak separation will rapidly become indistinct. In this case, only the total sum can be determined.

Further validation measurements were performed using the *Eracheck Pro* from eralytics® GmbH (Vienna, Austria), the benchtop infrared spectrometer with quantum cascade laser (IR-QCL) previously described in Chapter 3 (Section 3.4). Its measurement range extends from 0.5 to 2000 mg / L with absorption at wavelengths from 1370 to 1380 cm^{-1} . The measurement principle applied is in accordance with ASTM D7678-11 [194]. Standard solutions of toluene and crude oil in cyclohexane at concentrations of 100 to 1000 mg / L were prepared and measured to yield a calibration curve (plotting absorption versus concentration). As the IR-QCL spectrometer specifically measures the bending vibrations of methyl-groups, any compounds that do not contain methyl-groups will not be detected. Furthermore, differentiation between aliphatic and aromatic hydrocarbons is not possible and the molecular weights of the compounds are not taken into account. Hence, calibration with a standard that resembles the crude oil composition with respect to the ratio of aromatic to aliphatic hydrocarbons is essential to achieve accurate measurement results. In the case of a sample composition that deviates significantly from that used during calibration, an error will be introduced to the contaminant concentration measured.

4.3.4 Experimental Procedure

In a first set of measurements, the standard solutions of decane and toluene in the two solvent mixtures prepared according to the procedure outlined above (concentrations as per Table 4.1) were analysed with the Spinsolve. The results obtained were then compared against expected gravimetric values.

Subsequently, the contaminated water samples were investigated applying the Advanced SPE-NMR methodology. An Ismatec REGLO-ICC four channel peristaltic pump was available to perform the steps of the SPE procedure. The steps conventionally applied in reversed-phase SPE, as presented in Figure 2.8, can be reduced to loading, flushing with air and elution as was demonstrated via optimisation measurements in the previous chapter (Section 3.10). Figure 4.3 shows a schematic of the updated and reduced SPE procedure as applied during the measurements presented here.

The SPE cartridges are loaded with 150 ml of contaminated water at a constant flow rate of 5 ml/min (step (1) in Figure 2.8). Any residual water remaining in the SPE sorbent material from the loading is then removed using compressed air (Step (2) as per Figure 2.8). The last step (step (3) in Figure 2.8) consists of eluting the contaminants retained in the sorbent with a suitable solvent. For the twofold Advanced SPE-NMR procedure, two cartridges were loaded at the same time and the hydrocarbon contaminants subsequently eluted with 10 ml of the NMR solvent mixture 1 and 2, respectively. The solvent extracts were then measured and analysed using the ^1H NMR procedure

Figure 4.3 Experimental procedure for reversed-phase SPE of hydrocarbon content from an aqueous bulk phase. The procedure consists of (1) Loading (2) Flushing with compressed air and (3) Elution.

detailed above. For validation purposes of the Advanced SPE-NMR measurements, separate solid-phase extraction (same conditions) was performed and analysed with both IR-QCL and GC-FID. One SPE cartridge was used with an applied elution volume of 12 ml cyclohexane. The slightly increased elution volume (as compared to the SPE-NMR procedure) was necessary in this case to provide sufficient solvent extract to perform both analysis methods. The aim was to minimise the time delay between SPE and measurement, however, access to the GC-FID was limited and consequently a longer delay was inevitable. GC-FID measurements were performed altogether after finishing all required IR-QCL and NMR measurements. Triplicate analysis was done for all measurements.

4.4 Results and Discussion

With the intention of validating the applicability of the Advanced SPE-NMR approach to quantify aromatic and aliphatic hydrocarbons in the same sample, standard solutions were measured. In this context, the uncertainty related to the qNMR analysis was estimated. Progressing on from measurement validation, contaminated water samples were analysed applying the Advanced SPE-NMR methodology as well as the alternative methods. In the following sections, the results are presented and discussed in detail.

4.4.1 Measurement Validation

Table 4.1 above details the nine samples prepared to be measured using the Advanced SPE-NMR procedure in order to establish the linearity of the approach over the range of 191 to 1314 mg/L total oil in solvent. Total oil content as well as individual concentrations of toluene and decane were determined. Figure 4.4 shows the total oil concentration in the solvent as measured using the Advanced SPE-NMR methodology versus the expected gravimetric concentration. The dashed line indicates what would represent perfect agreement.

Figure 4.4 Measured total oil concentration (toluene and decane) using qNMR analysis versus expected gravimetric concentration. The expanded uncertainty at a confidence level of 95 % is shown as error bars for the Advanced SPE-NMR approach and shaded area for the gravimetric sample preparation. The line of equivalence $y = x$ is displayed as a dashed line (---).

It can be concluded from Figure 4.4 that no systematic error as a function of concentration is present. The relationship between the qNMR results ($c(\text{total oil}, \text{NMR})$) and the gravimetric concentrations ($c(\text{total oil}, \text{gravimetric})$) is linear with a correlation coefficient $r^2 = 0.991$. The uncertainty related to gravimetric sample preparation at a confidence level of 95 % is shown as a shaded area in Figure 4.4, whereas the error bars on each measurement represent the uncertainty related to the Advanced SPE-NMR analysis (also at a confidence level of 95 %). In general, the measurements are in good agreement with the gravimetric values.

With respect to individually quantifying the toluene and decane content in the standard solutions, the corresponding measurements are displayed in Figure 4.5. In Figure 4.5a, the decane content in the solvent as measured with Advanced SPE-NMR analysis is plotted versus expected gravimetric concentration, whereas Figure 4.5b shows the same for toluene.

Figure 4.5 Concentrations of (a) decane and (b) toluene in the solvent as determined with Advanced SPE-NMR versus expected gravimetric values. The individual concentrations correspond to the total oil content shown in Figure 4.4. The expanded uncertainty at a confidence level of 95 % is represented as error bars and shaded area for the Advanced SPE-NMR methodology and sample preparation, respectively. The line of equivalence $y = x$ is shown as a dashed line (- -).

As is evident from Figure 4.5a, agreement is excellent for the decane content where the deviation between the Advanced SPE-NMR and the expected gravimetric concentration is consistent with the uncertainty ranges. The relative error for the determination of decane in the solvent applying the Advanced SPE-NMR analysis is between 2 and 3 % which compares well with the relative error associated with sample preparation at 1 to 4 %. With respect to the toluene concentrations, however, some divergence from the gravimetric values outside the uncertainty bounds is evident despite the relative error having the same order of magnitude. Due to its lower boiling point at 111 °C compared to decane at 174 °C, the toluene is more susceptible to evaporation during sample preparation. Furthermore, as mentioned previously, the values of r_1 and r_2 deployed for these measurements are starting values only. Optimisation with regards to their collective sensitivity to aromatic and aliphatic content and subsequent measurements is required. This is detailed further below in Section 4.4.3.

4.4.2 Oil-in-water Analysis using Advanced SPE-NMR

After demonstrating that the Advanced SPE-NMR approach is viable to quantify the aromatic and aliphatic contribution to total oil content through the measurement of standard solutions, the applicability to contaminated water samples was investigated. Two batches, A and B, of crude oil and toluene dissolved in water were prepared as detailed above in Section 4.3.2. Sample batch A was deliberately prepared at a lower total oil concentration than batch B to confirm that the suggested methodology is suitable for quantification of varying contaminant concentration. Each batch was measured in three repetitions using Advanced SPE-NMR, SPE-IR-QCL and SPE-GC-FID. Calibration of the IR-QCL and GC-FID was performed prior to analysis with standard solutions of crude oil and toluene in cyclohexane (refer to Section 4.3.3).

Figure 4.6 Concentration of total oil water determined with Advanced SPE-NMR, SPE-IR-QCL and SPE-GC-FID. The individual measurements for both sample batches A and B are shown with the error bars representing the standard deviation across the repeated measurements with each method.

Figure 4.6 summarises the results obtained with the three applied methods for sample batch A and B. The measured concentrations of total oil using the Advanced SPE-NMR method, SPE-IR-QCL and SPE-GC-FID are shown for three samples each extracted from both samples. The error bars indicate the standard deviation across the triplicate measurement with the applied methods. The methods produce broadly consistent results, each reflecting the increased hydrocarbon content of sample batch B. However, the NMR methodology predicts a greater concentration than both GC-FID and IR-QCL. The IR-QCL measurements for sample batch B are significantly lower than the other two methods. This discrepancy was observed previously (refer to the proof of concept measurements in Chapter 3) and can be explained with the measurement principle of the IR-QCL instrument. Due to the narrow spectral width of the quantum cascade laser, the IR-QCL is exclusively sensitive to methyl groups and thus it is essential to perform calibration as accurately as possible with respect to the ratio between methylene and methyl groups. Reliable results with an established calibration can only be obtained as long as this ratio remains approximately consistent. However, with changing condition and increased total hydrocarbon content, the composition of the crude oil contaminants in the aqueous phase will inevitably change due to different water solubility of the compounds (i.e. aromatics versus aliphatics). Therefore, the ratio of methylene to methyl groups when dissolved in water changes with varying total oil concentration. This is the case with the samples presented in Figure 4.6. As is reported below (refer to Figure 4.9), the Advanced SPE-NMR and GC-FID measurements yield a ratio of aliphatics to aromatics in batch A of 0.69 and 0.71, respectively, whereas in batch B, values of 0.18 and 0.22, respectively, are determined. This highlights that in batch B, the aromatics contribute more to the

total oil content and consequently, the calibration of the IR-QCL (performed with approximately equal fractions of aromatics and aliphatics) is presumably not able to accurately quantify the contaminant concentration. With the reported ratio of aliphatics to aromatics in batch B, the results obtained from IR-QCL measurements can be corrected to reflect the increased aromatic content.

Figure 4.7 Raw and revised total oil concentration for sample batch B determined with SPE-IR-QCL in three measurements.

Figure 4.7 shows raw and revised total oil concentration for sample batch B determined with SPE-IR-QCL. As is indicated in Figure 4.7, the revised total oil concentration is approximately 17 mg/L higher than the raw results predict. This is a significant increase and highlights the importance of accurate calibration to achieve reliable results. Using the revised concentration to calculate an average total hydrocarbon content for sample batch B, good agreement across all three applied methods can be achieved. Figure 4.8 below summarises the average results of total oil content in samples A and B determined with Advanced SPE-NMR, SPE-GC-FID and revised SPE-IR-QCL for samples.

The revised IR-QCL analysis for batch B sits in between the NMR and GC results confirming that the correction according to the actual aliphatic/aromatic ratio is justified. However, the Advanced SPE-NMR measurements are slightly greater than both alternative methods. The deficits of the IR methodology regarding calibration, and consequences for the accuracy of obtained results, have been described above. With respect to the GC-FID, underestimation of total oil content might be caused by the experimental conditions as well as the analysis procedure. Due to restricted equipment access, a time delay was introduced between sample preparation and GC-FID analysis during which contaminant loss via evaporation is expected. In terms of the analysis procedure, establishing a

Figure 4.8 Average concentration of total oil in water as determined from the repeated measurements with Advanced SPE-NMR, SPE-IR-QCL and SPE-GC-FID. The measurement with IR-QCL on batch B is corrected to reflect the greater contribution of aromatic hydrocarbons to the total oil content. Error bars represent the standard deviation across the three measurements with each method.

suitable calibration is essential for accurate measurements and presumably the factor introducing most uncertainties. Calibration of the GC-FID was performed by obtaining chromatograms of standard solutions of crude oil in cyclohexane as well as toluene in cyclohexane. With respect to the crude oil solutions, the total peak area from C9 to C30 was integrated. The integral peak area was then plotted versus the gravimetric concentration to yield a calibration curve. On the assumption that the ratio of hydrocarbon with shorter chains, <C9, to those with longer chains, >C9, remains constant, the established calibration is then applied to actual samples. However, as with the IR-QCL, this is a crude assumption and should be taken into account for the interpretation and analysis of the results.

The analysis of the two samples A and B was extended with respect to the NMR and GC-FID results to extract the contributions of aromatic and aliphatic hydrocarbons to the total oil content. Figure 4.9 compares the measurements of both techniques in terms of total hydrocarbon as well as aromatic and aliphatic hydrocarbon concentration.

Figure 4.9 demonstrates good agreement regarding the relative amount of aromatic and aliphatic content in the sample. Agreement with respect to the actual amount can be considered reasonable. A much higher concentration of aromatic hydrocarbons is observed for sample B with both techniques. Due to the larger water solubility of aromatics as compared to that of aliphatics, the amount of aromatics actually dissolving the aqueous phase during sample preparation is appreciably higher. The water solubility of aliphatic hydrocarbons is limited and dependent on the chain length; the crude oil available for this study is expected to dissolve up to approximately 30 mg/L in water. This is

Figure 4.9 Concentration of total oil, aromatic and aliphatic hydrocarbons in two independent samples A and B as determined via ^1H NMR and GC-FID. Error bars represent the standard deviation across three measurements on the same sample.

confirmed with both ^1H NMR and GC-FID analysis which measure a relatively constant aliphatic content for both samples despite the higher amount of aliphatics added to sample B. The concentration of aromatic hydrocarbons significantly increases when more aromatics are added during sample preparation but is still less than the solubility limit at 500 to 600 mg/L. Consistent with the analysis shown previously, the NMR estimates a slightly higher content for both aromatic and aliphatic hydrocarbon content than GC-FID analysis.

For the measurements presented here, the composition of the aromatic contaminant, toluene, was known and thus the resonance of the methyl-group did not add to the aliphatic content. When dealing with actual produced water samples the exact composition of the aromatic hydrocarbons present in the sample will be unknown. Here, an assumption could be made regarding a prominent aromatic component of the relevant crude oil or the typical chemical structure regularly measured and subsequently a correction applied to the measurement. Likely aromatic contaminants are benzene and/or polycyclic aromatics [214], hence minimal or no reassignment would be required. Therefore, the error as a result of assuming that no aliphatic resonances are associated with aromatic content is relatively small. This needs to be investigated and quantified with crude oil that naturally contains aromatic components.

4.4.3 Optimisation of the Advanced SPE-NMR Methodology

As mentioned above, variation of r_1 and r_2 , hence the amounts of CHCl_3 and HMDSO added to the PCE solvent, can improve the sensitivity to aromatic and aliphatic content. In this context, theoretical optimisation can prove to be a useful tool to avoid an experimental trial and error approach.

Initially, a set of data was collected through repeated measurement of a selected model sample (sample #4 in Table 4.1) using the Advanced SPE-NMR methodology. The sample was prepared once, kept in a sealed NMR tube and ^1H NMR spectra taken repeatedly over a period of four days. Analysis to determine the contribution of aliphatic (decane) and aromatic (toluene) content in the sample was performed, the results are shown in Figure 4.10.

Figure 4.10 Concentrations of (a) decane and (b) toluene in the solvent measured over time with the Advanced SPE-NMR methodology using the starting ratios of HMDSO and CHCl_3 in the two solvent mixtures. The dashed lines indicate the average measurement of decane and toluene, respectively, across the repeated measurements.

The decane content as determined using the Advanced SPE-NMR approach is constant over time only showing slight variations across the repeated measurements ($\pm 6\%$). As is obvious from Figure 4.10b, the values determined for the toluene fraction vary greatly at $\pm 24\%$. The values deviate randomly, hence the possibility of a systematic error can be eliminated. Post-processing of the data, specifically phasing of the NMR spectra, as well as sample storage are potential sources of error. However, it was confirmed that slight variations in the post-processing do not cause such a significant variation and the samples were stored sealed with a cap to prevent loss of the analytes through evaporation. It was thus concluded that the starting values for the reference ratios do not provide sufficient sensitivity to both aromatic and aliphatic content.

Consequently, an optimisation problem was defined on the basis of the data shown in Figure 4.10 to solve for the concentrations of CHCl_3 and HMDSO that yield adequate sensitivity to both aromatics and aliphatics. The standard deviation across the repeated measurements for the decane and toluene content, respectively, was calculated and summed. The sum of the standard deviations posed

the objective function to be minimised:

$$\text{Minimise } z = \sigma(\text{toluene}) + \sigma(\text{decane}) \quad (4.6)$$

The decision variables to the objective function are the concentrations of CHCl_3 and HMDSO in solvent mixtures 1 and 2 and are subject to the following constraints:

$$\begin{aligned} 0.01 \text{ v/v \%} &\leq c_{\text{CHCl}_3,1} \leq 2.5 \text{ v/v \%} \\ 0.01 \text{ v/v \%} &\leq c_{\text{HMDSO},1} \\ 0.01 \text{ v/v \%} &\leq c_{\text{CHCl}_3,2} \leq 4 \text{ v/v \%} \\ 0.05 \text{ v/v \%} &\leq c_{\text{HMDSO},2} \end{aligned} \quad (4.7)$$

Herein, the indices 1 and 2 correspond to the solvent mixtures 1 and 2, respectively. Referring back to Equation 4.3, increasing the difference between r_1 and r_2 will enhance the sensitivity of the analysis. Consequently, the concentration of the reference compounds needs to be limited by finite values to enable a real solution to the optimisation problem. The specific values presented in Equation 4.7 were chosen in terms of sample preparation and resulting peak amplitudes. For accurate quantification, the reference resonances should be of the same order of magnitude as the target resonances. Furthermore, the ratios shall be different for the two solvent mixtures. The problem was solved using the GRG Nonlinear engine in Excel and the optimal solution was found to be:

$$\begin{aligned} c_{\text{CHCl}_3,1} &= 2.5 \text{ v/v \%} \\ c_{\text{HMDSO},1} &= 0.55 \text{ v/v \%} \\ c_{\text{CHCl}_3,2} &= 4 \text{ v/v \%} \\ c_{\text{HMDSO},2} &= 0.05 \text{ v/v \%} \end{aligned} \quad (4.8)$$

The theoretically optimised ratios were then tested by means of measurements to see if the sensitivity of the Advanced SPE-NMR methodology was improved. Again, two solvent mixtures were prepared by adding CHCl_3 and HMDSO to the PCE solvent at the optimised concentration values. The optimised solvent mixtures 1 and 2 contained 2.5 and 4 v/v % CHCl_3 as well as 0.55 and 0.05 v/v % HMDSO, respectively. Standard solutions of decane and toluene in the solvent mixtures were formulated in accordance with the concentrations detailed in Table 4.1 above and then analysed.

Figure 4.11 shows the total oil concentration in the solvent as measured using the Advanced SPE-NMR methodology with the optimised solvent ratios versus the expected gravimetric concentration. The dashed line indicates what would represent perfect agreement.

As can be seen, agreement between gravimetric and measured values is good and, when compared to the results obtained with the initial solvent ratios shown in Figure 4.4 above, the divergence is reduced significantly. The average deviation between the expected and measured values of total oil

Figure 4.11 Measured total oil concentration (toluene and decane) using qNMR analysis versus expected gravimetric concentration. For qNMR analysis, the ratios of HMDSO and CHCl_3 in the two solvent mixtures were optimised to increase the collective sensitivity of the measurement. The expanded uncertainty at a confidence level of 95 % is shown as error bars for the NMR results and shaded area for the gravimetric sample preparation. The line of equivalence $y = x$ is displayed as a dashed line (---).

over the range 191 to 2869 mg/L with the initial solvent ratios was determined to be 16 % (refer to Figure 4.4). This could be improved to 8 % deviation using the theoretically optimised solvent ratios (Figure 4.11). Again, the individual contributions of decane and toluene were extracted from the total oil concentration to investigate the agreement between gravimetric and measured values. Figures 4.12a and 4.12b show the decane and toluene content, respectively, as measured with Advanced SPE-NMR plotted versus expected gravimetric concentration.

Again, agreement for decane is excellent, which is reflected in the average deviation between gravimetric and measured concentration of 8 % (the same as previously for the results shown in Figure 4.5a). The sensitivity of the Advanced SPE-NMR methodology with respect to the estimation of the toluene content was significantly enhanced using the optimised solvent ratios. Initially, an average deviation of 24 % was established (Figure 4.5b), whereas the results demonstrated in Figure 4.12b yield an average divergence between gravimetric and measured values of 10 % over the concentration range of 104 to 1555 mg/L toluene in solvent.

Repeatability of the measurements with Advanced SPE-NMR was also tested. For this, two random samples of the standard solutions (Table 4.1) prepared with the optimised solvent ratios were measured repeatedly over the course of 6 days. The samples were kept in capped NMR tubes and ^1H NMR spectra taken at varying time intervals. The measurement of the original solvent mixtures without added contaminants was not repeated.

Figure 4.12 Concentrations of (a) decane and (b) toluene in the solvent — extracted from the total oil content shown in Figure 4.11 — as determined with Advanced SPE-NMR versus expected gravimetric values. Herein, the ratios of HMDSO and CHCl_3 in the two solvent mixtures were optimised to increase the sensitivity of the measurement. The expanded uncertainty at a confidence level of 95 % is represented as error bars and shaded area for the Advanced SPE-NMR methodology and sample preparation, respectively. The line of equivalence $y = x$ is shown as a dashed line (---).

The individual concentrations of decane and toluene were extracted from the total oil content to investigate the variability over time. Figure 4.13 below shows the decane and toluene content in the two independent samples over time as well as the average value determined from the repeated measurements.

Figure 4.13 Concentrations of (a) decane and (b) toluene in two standard samples measured over time with the Advanced SPE-NMR methodology. Herein, the ratios of HMDSO and CHCl_3 in the two solvent mixtures have been optimised to increase the sensitivity of the measurement. The dashed lines indicate the average measurement of decane and toluene, respectively, across the repeated measurements.

Repeatability of the decane measurement is good, the variation is determined to be $\pm 5 \%$ and $\pm 6 \%$ for the lower and higher concentrated sample, respectively. The toluene content varies slightly more at $\pm 10 \%$ for both samples. However, this compares favourably to the repeatability measurement

performed previously with the initial solvent ratios shown in Figure 4.10 where the variation of decane was the same at $\pm 6\%$, but the toluene content varied $\pm 24\%$ for the respective sample. The collective repeatability of total oil concentration was consequently also improved, the variability was reduced from $\pm 18\%$ to ± 6 and $\pm 7\%$, respectively. A significant improvement was achieved through optimisation of the solvent mixtures in terms of measurement repeatability.

4.5 Conclusion

The SPE-NMR methodology developed for the quantitative analysis of produced water with respect to total oil content was extended to explore the possibility of separate quantification of the aromatic and aliphatic contribution. The novel NMR approach, referred to as Advanced SPE-NMR, is compatible with a benchtop ^1H NMR apparatus and allows the simultaneous assessment of aromatic and aliphatic hydrocarbon content in the same sample.

The fundamental principle of the Advanced SPE-NMR methodology is the application of two solvent mixtures with two different reference compounds. The ratio of the two reference compounds is different in the two mixtures. By using the ratio of the integral areas of the two reference compounds in each mixture, the measurement is rendered self-calibrating.

Choosing decane and toluene as model compounds for aromatic and aliphatic hydrocarbons present in crude oil, standard solutions covering a concentration range of 191 to 2869 mg/L total oil in the solvent were prepared and measured with Advanced SPE-NMR analysis to validate the methodology. The initially selected solvent ratios showed to provide reasonably good agreement between expected gravimetric and measured values with respect to total oil. Agreement for the decane content was excellent, however, the toluene showed some random variation over the chosen concentration range. Through optimisation of the solvent ratios, this variation and the deviation of the values obtained with Advanced SPE-NMR analysis versus the gravimetric concentration were significantly reduced. Overall, with optimised solvent ratios, the agreement for total oil as well as individual decane and toluene content between gravimetric and measured values was demonstrated to be good and the measurement uncertainty comparable to the accuracy with which the samples can be prepared.

The proposed methodology was further applied to water samples contaminated with a light crude oil (mainly aliphatics) and toluene (as a representative of aromatics that can be present in crude oil). The Advanced SPE-NMR measurements were validated against SPE-IR-QCL and -GC-FID analysis and good agreement was achieved. Separation of the total oil content in the samples into aromatic and aliphatic hydrocarbons and quantification thereof was performed via Advanced SPE-NMR and SPE-GC-FID analysis. Again, the qNMR analysis showed to be feasible in this respect and compared well against GC-FID analysis.

It was shown that the proposed Advanced SPE-NMR analysis is able to accurately determine ppm concentrations of aromatic and aliphatic hydrocarbons in both solvent and water samples. This measurement approach will potentially be attractive for the oil and gas industry as legislation with respect to the discharge limit of produced water is increasingly stringent and focused on toxicity. Application of the Advanced SPE-NMR methodology to specifically determine the contribution of aromatics to total oil in produced water discharge streams allows a better estimation of the actual toxicity to aquatic life given that the water solubility and persistence of aromatics is greater than those of the aliphatic hydrocarbons.

Chapter 5

SPE-NMR Prototype Design, Development and Automation

The ultimate objective of this doctoral research was the development and subsequent testing of a working prototype that implements the SPE-NMR approach as a (semi) automated option for quantitative produced water analysis. As is described in the previous chapters, the first step in this regard was to apply the methodology in the laboratory to demonstrate its suitability to analyse the oil content in water at the ppm level. Initially, a mostly manual approach was used for sample preparation and measurement. The next step was the design and development of a working prototype that implements the SPE procedure and subsequently performs an in-line NMR measurement combined with automated data analysis. This chapter describes the design considerations (Section 5.1) and development (Section 5.2) of such a prototype. The first version of the prototype remained semi-automated for tests of functionality and trialling under field conditions. Subsequently, Section 5.3 describes the setup of an in-line NMR measurement and the advancement of the semi-automated prototype to a fully automated prototype that implements the SPE-NMR methodology.

5.1 Design

A suitable prototype implementing the SPE-NMR methodology must be able to demonstrate its feasibility for OiW analysis and the potential to be commercialised as a laboratory and field device, for onshore, offshore and subsea application. Both the offshore and subsea application pose significant challenges with respect to the design of a metering device due to their harsh environments. The SPE-NMR prototype developed as part of this doctoral research is not required to qualify for such application in the short term. Validation of its capabilities for onshore deployment are prioritised given that the industry has yet to commonly adopt subsea processing and separation. However, the

long term objective is to show the capabilities and potential of SPE-NMR to be eventually developed into a device that can withstand and operate reliably in subsea conditions.

During the process of designing a suitable approach for the implementation of the SPE-NMR methodology in the form of an automated prototype, both the intermediate and ultimate objective, onshore and subsea application, respectively, have to be considered. Generally, oil-in-water measurements can be carried out as a benchtop application (requiring sampling from the produced water stream), a by-line or on-line measurement. Benchtop instruments are readily available and well established for the measurement of oil-in-water in the field, for example the Horiba instrument is widely applied on offshore platforms for the determination of OG and TPH according to ASTM 7066-04 [32]. However, manual sampling from the process stream is required and the measurements are generally more time-intensive due to the manual sample preparation involved. On-line sensors on the other hand are applied directly on the process stream and provide regular measurements without manual interference. Similarly, sensors installed on a bypass line supply measurement results automatically and without the need of manual sampling or sample preparation. As opposed to an on-line sensor, a bypass sensor is usually unable to cope with the conditions in the process streams and hence a bypass line is used to perform the measurements under controlled conditions. In the context of the application of SPE-NMR in the field, implementation as an on-line sensor is not viable. Here, the SPE procedure is the limiting factor as maximum flow rate allowed is 5 ml/min. The produced water stream is expected to flow at pressures up to 350 bar and with velocities that exceed what is acceptable for the SPE procedure [40]. Furthermore, due to the different steps that need to be performed during SPE, a bypass line is necessary for the SPE-NMR approach. Therefore, it is proposed to develop the SPE-NMR methodology as an ancillary device to be deployed in conjunction with an on-line sensor. Due to the self-calibrating character of the SPE-NMR measurement, it could signal the necessity to (re-)calibrate the on-line sensor or indicate issues with the on-line reading, for example due to the presence of production chemicals. A SPE-NMR monitor can essentially operate as a backup and validation to an installed on-line sensor to provide regular measurements confirming the on-line readings. Proposing the installation of a bypass backup SPE-NMR measurement in combination with an on-line, optical sensor (i.e. UV fluorescence or similar) is expected to facilitate regulatory approval for discharge of produced water at remote locations, i.e. on unmanned platforms or subsea.

As a bypass measurement, the produced water stream can be regulated to comply with the requirements for the SPE procedure by means of a simple flow control valve. Once the produced water has passed through the SPE sorbent material during the loading step, it can be discharged. The solvent, on the other hand, cannot be discharged and should be reused in order to extend the lifetime of the apparatus. Further considerations and details regarding the design of the flow path of the prototype are described below.

5.1.1 Requirements

In the following section, the technical requirements for a working prototype implementing the SPE-NMR approach for produced water analysis are defined. Note that these are in the context of benchtop laboratory and onshore field application only; for a subsea device, more specific demands according to the harsh surrounding conditions and requirements regarding maintenance access have to be met. Technical requirements for such subsea oil-in-water sensors were formulated as part of the RPSEA Project "Subsea Produced Water Sensor Development"[46, 40]. For a functional benchtop SPE-NMR prototype, the requirements were specified in respect of proof-of-concept testing and potential of the device to be further developed for subsea application at a later stage:

- Automated SPE procedure and subsequent NMR measurement including data analysis.
- Measurements provided once per hour.
- Design limits regarding the produced water: 0 - 100 mg/L of oil contamination, oils covering a range of API gravities (0.93 - 0.73 kg / m³), varying salinity of the brine.
- Operating environment: 5 - 50°C, ambient pressure.
- Fluid temperature: 3 - 95 °C.
- System pressure: 1 - 40 bar.
- Ultimately, the sensor must be designed for 20 years lifetime and a mean time between failure/maintenance of 5 years. Thus, the prototype developed as part of this work shall present feasible options for upscaling.
- SPE-NMR measurements validated against well-established, alternative oil-in-water analysis methods.

A novel oil-in-water monitor needs to be certified according to the regulations relevant at the location of application. In Australia or the North Sea, for acceptance to be applied in the field, a new methodology needs to be validated against the OSPAR reference method which uses GC-FID as the analysis tool [14]. For validation testing in a laboratory environment or during a field trial, it is legitimate to use other well-established measurement methods to compare the new method against and demonstrate its applicability.

The methodology of SPE-NMR has the advantage of addressing all hydrocarbon contaminants that are extracted during the SPE procedure, in the dissolved and/or dispersed state. Salinity and suspended solids can become a challenge due to potential deposition in the sorbent material. Robustness to solids and potential effects on the prototype, specifically on the SPE cartridges, will be

the subject of extensive laboratory testing in the future. It is not expected that solids or salinity have an adverse impact on the measurements themselves since NMR is a non-optical measurement.

The NMR spectrometer Spinsolve is currently tuned to laboratory conditions. The magnet shows best performance at 20 to 25 °C and relative humidity should be between 20 and 85 %, non-condensing. However, the magnet can be tuned to operate at a different temperature. In fact, it is assumed that the spectrometer works more stable at remote locations, specifically subsea, where temperature fluctuations are minimal and electrical noise will be significantly lower than topside or onshore.

Lifetime and autonomy of the oil-in-water sensor needs to be maximised as any intervention once post-installation, either for repair or re-calibration, is time-intensive and can be costly, especially in the context of a subsea device. With respect to a SPE-NMR apparatus, the critical aspects are the SPE cartridges and the solvent supply. Measurements to investigate the reusability of cartridges and solvent are essential for scale-up and estimation of maximum operating time without intervention. These will be detailed in Chapter 6.

Upon the basis of the technical requirements of the SPE-NMR measurement and the components for the construction of a prototype, potential designs were considered and tested in terms of applicability and functionality.

5.1.2 Model Description

Prior to establishing a design for the development of a SPE-NMR prototype, similar instruments that are applied in other fields were reviewed. In this context, research was carried out on a discontinued Supercritical Fluid Extraction (SFE) system originally built and sold by Hewlett Packard. The SFE procedure has similarities with SPE, such as the use of extraction cartridges and multiple stages that apply the sample and subsequently solvents to extract the analyte of interest. Furthermore, the commercialised apparatus operates at high pressures and is automated. One of these SFE instruments was available for this doctoral research to be used for testing and as a model system for the design of a SPE-NMR prototype. Figure 5.1 shows the SFE system and a High Pressure Liquid Chromatography (HPLC) pump that was used for sample loading.

As can be seen in Figure 5.1, the SFE apparatus incorporates a sample carousel that can accommodate eight cartridges and, through the help of motors and controlled via a computer program, moves up and down to connect/disconnect the cartridges in the extraction chamber (SFE chamber). Furthermore, a small pump is located at the back of the system (not visible in Figure 5.1); this was used to pump the elution solvent. To allow for the implementation of the SPE procedure for produced water analysis, the SFE system was complemented with an additional pump for the loading step and a high pressure air line to enable flushing of the cartridge with compressed air.

Figure 5.1 Supercritical Fluid Extractor System HP 7680T and HPLC pump used for very initial testing of automated SPE for produced water analysis.

Sorbent material from the silica based, octadecyl SPE cartridges Prevail C18 was transferred to cartridges inherent to the SFE system. A sample of hexane dissolved in water was then prepared at low concentration and left overnight to equilibrate. Subsequently, the SPE procedure was carried out using the SFE apparatus and HPLC pump. Due to the low concentration, a slightly higher loading volume was selected, 400 and 500 ml for run 1 and 2, respectively. The elution volume was also increased to ensure that all contaminants are extracted from the sorbent material. Volumes of 24 and 19 ml (values arbitrarily chosen) were applied for run 1 and 2, respectively. The obtained samples were measured using the usual NMR pulse-and-collect sequence with the 1 Tesla spectrometer. The frequency domain spectra of hexane in the extraction solvent obtained with the 1 Tesla are shown in Figure 5.2.

None of the two spectra present any visible contamination and the peak magnitudes are similar. From the two spectra, the concentration of hexane in the sample was derived using the quantitative NMR methodology developed in the context of this doctoral research (refer to Chapters 2 and 3). For validation purposes, the hexane-in-water sample was also analysed using the GC-MS method as outlined in Chapter 3. A time delay of two days between sampling and GC-MS analysis was introduced because of restricted equipment access. Table 5.1 summarises the hexane-in-water concentrations determined with the two methods, where the GC-MS result is averaged over five measurements of the sample.

Figure 5.2 ^1H NMR spectra of hexane (peak 1) in the 1% v/v CHCl_3 (peak 2) in PCE solvent after solid-phase extraction using the modified SFE system. Two SPE procedures were carried out, the resulting frequency domain spectra from run 1 and 2 are displayed.

A decrease in concentration is observed with the maximum measured in run 1 with SPE-NMR and the minimum with the GC-MS. This is attributed to contaminant loss through evaporation over the course of the measurements which is further pronounced for the GC-MS analysis as this was conducted two days after sample extraction. The averages of $c_{\text{hexane},\text{NMR}} = 3.9 \pm 1.1$ mg/L and $c_{\text{hexane},\text{GC-MS}} = 2.8 \pm 0.8$ mg/L, however, agree well and demonstrate the ability to perform the SPE for produced water analysis in an automated procedure.

Table 5.1 Concentration of hexane in water determined via SPE-NMR using the SFE system and GC-MS.

Run no.	Hexane-in-water [mg/L]	
	SPE-NMR (SFE)	GC-MS
1	4.7	2.8
2	3.1	

With the intention to learn from an apparatus that has been shown to work, the SFE system HP 7680T was used as a model to start the design of an SPE-NMR apparatus. A detailed description of the design approach and resulting flow diagram is given in the following section.

5.1.3 Design Solution SPE Device

The cartridge carousel and connection mechanism of the HP 7680T instrument are the most relevant parts with respect to building a similar apparatus. The carousel facilitates automatic selection and replacement of cartridges to conduct a measurement. A simplified schematic of the carousel and connectors is shown in Figure 5.1 below.

Figure 5.3 Basic schematic of the sample carousel, connectors and motors of the HP 7680T SFE apparatus. A photo of the cartridges belonging to the system is also shown.

Via a computer program, a cartridge position can be selected, which consequently initiates rotation of the carousel in order to put the selected cartridge into position. Then, a connection can be established. A connector is moved upwards by a motor, pushing the selected cartridge into the extraction chamber and against the correspondent connector. On both sides, a needle inserts into the cartridge cap enabling in- and outflow of the cartridge. The concept of the cartridges and the connectors is taken on for the design of the SPE device in the context of this doctoral research. However, instead of a rotating carousel, a sample platform that moves horizontally, driven by a simple linear actuator, is preferred. Rotary motion is generally associated with more wear and less precision regarding position control. For horizontal movement of a sample platform, a simple stepper motor in combination with a lead screw can be used to create forwards and backwards motion. This provides highly repeatable movement, long operational life and sufficient position accuracy. Furthermore, a platform that moves linearly along one axis is readily extended to accommodate more samples by adding another dimension, for example a second row that can be selected by movement perpendicular to the main axis. Instead of the lower connector lifting a cartridge and pushing it towards the upper, stationary

connector, both connectors will be moving in the modified design solution. Thereby, the cartridges will be fixed on the platform and no guide or chamber is required. The design of the modified sample carousel as a platform that moves horizontally is schematically shown in Figure 5.4.

Figure 5.4 Basic schematic of the sample platform, connectors and motors of the new design enabling horizontal movement of the platform and vertical movement of both connectors.

The design of the connectors and mating cartridges plus caps was adopted for the development of an SPE device, but slightly modified to fit the purpose. The cartridge body was reduced in size as a sorbent bed of approximately 800 to 900 mg, similar to the commercial Prevail C18 cartridges, was targeted. The caps were made from metal with slightly different threads to achieve a tight seal. The cartridge caps for the HP 7680T system contain a sintered metal filter. Flow is directed from the needle through the filter into the cartridge at the inlet (top) and vice versa at the outlet (bottom). For ease of manufacturing, these inserts are incorporated in the new design and used inside the metal cartridge caps (the metal caps replace the plastic caps from the original cartridges). Figure 5.5 shows the two different cartridge caps, the cartridges and one of the connector tips built for the SPE device.

To be able to move the connectors and the sample platform, robust linear motion rails can be used. These can be actuated with simple stepper motors. Movement of the vertical motors has to be stopped as soon as a flush connection between the cartridge (cap) and the connector tip has been established. This can be done via measurement of the force exerted onto the cap. The details regarding the selected components and the operating principle of the SPE device are provided below in Section 5.2.

Figure 5.5 Photos of the SPE cartridges and connector built for the SPE device. The left photo shows the stainless steel cartridges with the original plastic caps (left) and new brass caps (right) installed on the platform. The top connector with needle that inserts into the caps is also visible. The right photo shows the mated connector and cartridge with the needle inserted into the cartridge cap.

5.2 Prototype Development and Construction

The design and construction of the semi-automated prototype for implementation of SPE-NMR measurements is the subject of the following sections. A description of the design solution and actual construction of the prototype including the electronics and software development are given along with some initial test results generated in the laboratory.

5.2.1 Design and Construction of the Prototype

Designing a suitable process flow diagram (PFD) for the SPE-NMR prototype was the first step in the development phase. All desired operations for the SPE procedure and NMR measurements have to be considered. It is important that the aqueous stream (produced water) and the solvent have an individual flow path both through the SPE cartridges and then through the NMR spectrometer to enable magnet shimming with the clean water and, during elution, NMR measurement of the resulting solvent extract. Furthermore, a path for direct measurement of either fluid without passing through the cartridges is required; the produced water sample needs to be checked for oil spikes and baseline measurements of the solvent need to be obtained in the case of solvent recycling. The aqueous waste container and recycling path for the elution solvent have to be kept separate in order to avoid discharging halogenated solvent with the waste water.

In terms of valves to direct the fluid flow and keep the aqueous and solvent streams separate where necessary, 2-way and 3-way valves were considered. The latter are the more viable option in terms of reducing the number of incorporated components and require less digital lines for control.

Figure 5.6 PFD of the SPE and NMR analysis procedure for automated oil-in-water measurements. MFC = mass flow controller, V1 - V6 = electrically actuated ball valves, P1 and P2 = piston pumps for solvent and sample, respectively.

The SPE device was developed and built by the Mechanical Workshop at UWA according to the design schematic shown in Figure 5.7.

Figure 5.7 3D schematic of the SPE device as developed by the UWA Mechanical Workshop.

5.2 Prototype Development and Construction

Where possible, commercial components were used to simplify the construction process. Furthermore, exploitation of commercial products facilitates replication of the system, a significant factor for potential future commercialisation of the working SPE-NMR prototype.

As discussed above, it was decided to use a linear moving platform that accommodates the SPE cartridges. Three linear motion rails were purchased along with three simple stepper motors for actuation. In order to monitor the connection between cartridge cap and connector tip, two commercial load cells, s-beam type, were installed as part of the connectors. The top connector including the load cell (red/black/yellow) can be seen in Figure 5.8a.

Figure 5.8 Parts of the sampling device built by the UWA Mechanical Workshop. (a) Top connector and installed load cell. A flush connection between the connector tip and the cartridge cap is established. (b) Home position limit switch of the horizontal motor.

As soon as a flush connection is successfully established (as is demonstrated in Figure 5.8a), which is determined with the help of the load cells, the motors are stopped. Similar to the limit switches (example shown in Figure 5.8b) that are mounted to the linear rails — one each for the home position and one for end-of-travel —, this is a hardware stop to enable instant stoppage.

The linear rails, motors, load cells and platform are mounted onto a sturdy aluminium frame. The frame supports the weight of the components and provides sufficient stability during movement. Furthermore, it is readily mounted onto a substructure, as is required for this prototype. The SPE-NMR prototype needs to be mobile, hence all the equipment is mounted onto a two-tier, custom built trolley (UWA Mechanical Workshop). The top tier accommodates the SPE device including all required electronics. A fold-out table provides space for a laptop to control the process. In order to automatically perform the SPE procedure using the SPE device, pumps, a compressed air supply, valves, tubing and supply containers are required. Market research was performed and the components selected according to the best price-performance ratio. The additional instruments and components along with supply and waste containers are fixed to the bottom tier. Figure 5.9 shows

both the top part of the trolley (Figure 5.9a) accommodating the SPE device and some electronics as well as the bottom compartment (Figure 5.9b) with the utilities. A photo of the entire mobile SPE device, referred to as the Self-Contained Transportable (SCT), can be seen in Figure 5.9c complete with a laptop to operate the system.

Figure 5.9 The SCT in the UWA laboratory accommodating the SPE device, electronics and equipment to perform automated solid-phase extraction controlled via a computer. (a) Top and (b) bottom part of the Self-Contained Transportable and (c) complete system as set up in the laboratory.

Removable polycarbonate shields are available that can be attached to the sides of the bottom compartment and, in the form of a box with sliding doors, put over the SPE device on the top part of the trolley. Access for power supply, cabling and the compressed air line is provided.

The design concept (PFD shown in Figure 5.6) of the SCT includes the prerequisites to connect the benchtop NMR spectrometer to the prototype in order to provide a fully automated measurement.

Initially, the NMR measurement was conducted separately to allow troubleshooting and optimisation before progressing to full automation. The setup of the Spinsolve NMR spectrometer as an in-line measurement to form part of the prototype is described in more detail in Section 5.3 below.

5.2.2 Electronics

The electronics hardware to power the individual components of the SCT and enable control via a computer was built in-house by Dr. John Zhen (electronics engineer). The hardware consists of one control box that contains the LabVIEW interface, one break-out box with relays and power supply lines for the valves, the pumps and the mass flow controller and two additional boxes, one for the motors' power supply and drivers and the other one to house the transmitters for the two load cells. The schematic in Figure 5.10 provides a comprehensive overview of the electronics layout for the SCT.

Figure 5.10 Layout of the electronics hardware providing the power supply for the components of the SCT and distributing digital input and output lines to control the system via computer.

Interfacing between the instruments and the computer is facilitated with a 24 channel USB controller and custom-built hardware providing 5 VDC (Volt Direct Current) and 24 VDC output lines as well

as feedback (input) lines. The modular systems commercially available from National Instruments have a common voltage source (if one fails, all fail), a maximum current output of 1 A (Ampere) and fixed 24 V outputs only. Thereby, these systems were considered unsuitable in the context of this application. The control box custom built for the SCT uses a simple USB controller that can send and receive digital signals. A total of 24 channels is available of which 20 are configured as digital output (sending signals), three are digital input (receiving digital signals) and one is a counter input port. The final layout of the channels and corresponding functions are listed in Table 5.2.

Table 5.2 Channel layout regarding the digital input/output and corresponding functions of the interface between LabVIEW and the SCT.

Channel #	Instrument/Function	Details
1	Sample pump	On/off
2	Clock output	Enable clock to drive stepper motors
3	Enable motor x	Provides power to motor x
4	Enable motor y	Provides power to motor y
5	Enable motor z	Provides power to motor z
6	Direction motor x	Forwards/backwards
7	Direction motor y	Forwards/backwards
8	Spinsolve valve	
9	MFC	On/off
10	Solvent pump	On/off
11	Valve #1	Switch between positions A and B
12	Valve #2	Switch between positions A and B
13	Valve #3	Switch between positions A and B
14	Valve #4	Switch between positions A and B
15	Valve #5	Switch between positions A and B
16	Valve #6	Switch between positions A and B
17	Direction motor z	Forwards/backwards
18	Override limit switch	Override limit switch hardware stop
19	Override y	Override the hardware stop from load cell y
20	Override z	Override the hardware stop from load cell z
21	Feedback limit switches	Receive feedback signal from limit switches (one channel only)
22	Feedback load cell y	Receive feedback signal from load cell y (top)
23	Feedback load cell z	Receive feedback signal from load cell z (bottom)
24	Counter input	Reads a digital clock signal

As detailed in Figure 5.10 above, the flow rate of the two pumps and the mass flow controller (MFC) is adjusted with the voltage supplied to the instruments. The two liquid pumps are provided with a fixed voltage that results in a 5 ml/min flow rate. The MFC voltage is set to give maximum output, hence the output pressure equals the inlet pressure. Compressed air is supplied from a gas cylinder with a gauge pressure of approximately 200 bar. The maximum inlet pressure for the MFC is 35 bar, a regulator is installed between the gas cylinder and MFC to meet this requirement. By adjusting the regulator to provide a pressure between 1 and 35 bar, the user can control the pressure of the air that is delivered via the MFC to the system. For a permanent setup, the inlet pressure of the MFC would be set to the maximum, 35 bar, and the pressure delivered to the system fine-tuned with the MFC.

The load cells have a capacity of 50 lbs (22.7 kg) and are used to measure tension or compression forces. For the application as part of the cartridge connectors, only compression forces are of interest. The load cells are used to monitor the force exhibited when the connector tip pushes onto the cartridge cap. Once a pre-set limit is reached, a signal is sent that stops the motors. The transmitters are configured to output a voltage ranging from 0 to 5 V depending on the force that the load cell measures. The maximum force, 22.7 kg, results in maximum voltage output and the relevant motor is stopped immediately. Then, a digital signal is sent to the computer signalling that the cartridge is connected and the motor has stopped. It was opted to use a hardware trigger to ensure that motion is stopped instantly. Using a software program to stop the motors adds a time delay — the software has to receive an input signal and subsequently sent out an output signal to stop the motor — and has the potential of failure, for example if the program freezes or crashes. Once the motor is stopped as a consequence of the compressions force at the load cell, an override signal is needed to restart the motor despite the load cell signalling that the maximum force is (still) applied. Two digital output lines are configured to provide such override signal for the two load cells individually.

The limit switches are set up similarly to the load cells. As soon as a limit switch is hit, the relevant motors is stopped immediately and a signal is sent to the computer. Only one digital input line to communicate that a limit switch is triggered and only one digital output to send the override signal are available. The software program has to determine which limit switch is hit on the basis of the active motor and its direction. Again, a 'hardware stop' was preferred over a 'software' stop to ensure instant and fail-safe stoppage of motor movement.

The three-way valves selected for the SCT are supplied with 24 VDC via the break-out box. The default position of the valves is in *A*, providing a logic low via the digital output lines will switch the relevant valve to position *B*. The valves are configured to be continuously supplied with power as soon as the control box is switched on. If not otherwise specified by means of a digital signal, the valves will adopt their default position as soon as the power supply is on.

The three stepper motors have a separate power supply to provide 24 VDC. To initiate any movement three digital signals need to be sent via the control box: enable clock (channel # 2), enable motor (to select the motor, channels # 3, 4 or 5) and the direction (default is backwards, logic high).

A square wave pulse generator is built into the control box and the enable clock signal essentially transfers square wave pulses to drive the motors. Only one motor can run at a time.

According to the layout of the digital channels, a software program was developed in LabVIEW to control the instruments and monitor any feedback lines. Development of the program is detailed in Section 5.2.3 below.

5.2.3 Software Development with LabVIEW

Laboratory Virtual Instrument Engineering Workbench, LabVIEW, is a development environment from National Instrument that implements a graphical programming language to create virtual instruments. Virtual instrumentation is used to visualise an instrument or device or complete measurement setup on a computer. When applying LabVIEW combined with a data acquisition device and computer, the user can control instruments as well as collect, manipulate and display data. In LabVIEW, a circuit is constructed with the help of so-called Virtual Instruments (VIs), which are a graphical representation of physical instruments. LabVIEW provides a comprehensive set of pre-built VIs or the user can built custom-designed VIs in order to develop a program. Every VI has a front panel, that essentially represents the user interface, and a block diagram that contains the program code in the graphical programming language G. The block diagram of a LabVIEW application consists of structures, such as while-loops or event structures, functions and so called sub-VIs (VIs that are placed on the block diagram of another VI). The data flow between the components of an application is facilitated with wires, data flow always occurs from left to right.

The objectives of a software program for the SCT were the control of the instruments for the SPE procedure, operation of the NMR spectrometer and storage as well as post-processing and analysis of NMR spectra. The program should enable the user to control the steps for the measurements but also provide the option for further development into a sequence that carries out all required steps automatically. Thus, it was decided to develop a LabVIEW application in the form of an event-driven state machine. The main VI is called *DickeBerta* and consists of a front panel, the user interface, and the program code in the block diagram. Sub-VIs have been developed and added to the block diagram to facilitate control of the instruments, saving and reading data, performing NMR measurements, post-processing and analysis of NMR spectra and the display of any data or messages that are relevant to the user. In the following, a general overview of the program is given. A user manual is available (refer to Appendix B) that explains in more detail how to install, configure and use the software and also contains a high-level description of the program code. Documentation in the program itself, accessible via the context menu, provides information in regards to the individual sub-VIs and their functionalities.

The graphical user interface (GUI) of *DickeBerta* is shown in Figure 5.11 highlighting its main parts. The tab control provides the necessary controls to enable the user to operate the combined SCT

and NMR. The individual controls and functions are arranged into groups for reasons of clarity, e.g. in Figure 5.11, the data analysis tab, that performs post-processing of a NMR spectrum and calculates the concentration of oil-in-water of the specific sample, is selected. The digital output indicators are located to the left-hand side of the tab control. These show any active lines indicating which instruments/devices are currently in operation. Below the tab control, status indicators inform the user about the SPE procedure. On the right-hand side, the shutdown button as well as error information can be found.

Figure 5.11 Graphical user interface of DickeBerta.

The programming architecture behind the GUI consists of an event-driven state machine combined with a producer/consumer design. This is a more advanced version of the basic state machine that typically contains a set of defined states and a case selector to determine which state is executed next; the cases are automatically executed in sequence. In the context of this doctoral research, the implementation is a bit more complex as the program needs to react to user input as well as events generated within the program. This is enabled by means of an event structure, shown in Figure 5.12a, that captures any events that are generated by the user via the user interface or from within the program itself. These events then trigger the main loop (refer to Figure 5.12b) and determine which of the available cases is executed.

The main loop is essentially the producer of the state machine, as it not only performs sub-tasks (such as data analysis) but also controls three additional consumer loops. These are the digital output loop, the feedback loop and the counter input loop. A fifth loop is deployed for error handling, but does not directly respond to the main loop. Instead, it is supposed to catch any error that can occur

Figure 5.12 Examples of loops in the block diagram of DickeBerta. (a) Event structure that captures user events and events generated in the program. Consequently, the events trigger the (b) main loop that is responsible for execution of any sub-tasks and control of the data input and output loops.

within the other four loops, logs it to a text file and informs the user about the error/s. The digital output loop sends a logical high or low via the relevant digital output line in order to start, stop or direct any of the instruments. Feedback from the limit switches and load cells is received through the feedback loop and events are generated accordingly. The counter input loop provides a timer by counting the edges of a square wave when instructed by the main loop to do so.

The reader is referred to the program itself and contained context help as well as the user manual in Appendix B for instructions on how to use DickeBerta in order for control of the SCT and additional details regarding the program code. In the following, a comprehensive summary of the devices that are operated with DickeBerta is provided. Note that initially, the NMR spectrometer and hence the NMR measurements and data analysis were separate from the automatic SPE procedure using the SCT. This intermediate development stage was used to confirm the functionality of the semi-automated prototype before proceeding to add in-line NMR measurements.

A short summary of the abilities of the software application DickeBerta is given below:

- **Motor control:** One horizontal and two vertical motors can be initiated to move linear motion rails forwards or backwards. The horizontal motor moves a platform that accommodates SPE cartridges - it is possible to control the motor manually by hitting the stop button or a cartridge position can be selected and the program will stop the motor automatically when in position. The vertical motors are moved forwards to connect a cartridge and two load cells, one for each connector, are used to signal when a successful connection is established. Feedback from limit switches for end-of-travel and home position are monitored and displayed on the user interface. The home position limit switch is automatically reset, indicators on the user interface show which motor is currently at home. The position of the motors/linear rails is saved to a text file (configuration file) when the program is shutdown and consequently loaded upon start-up to pre-set the relevant indicators.
- **Pumps:** The two liquid pumps, for solvent and sample, are operated via their respective tab. A value for the volume is defined and the pump started. Through the use of the timer, which is implemented in the counter input loop on the block diagram, the pump is stopped after the desired volume has been pumped. This functionality is based on a constant flow rate of the pumps (set to 5 ml/min).
- **Valves:** The six three-way ball and one two-way solenoid valves are operated on the valve tab. The three-way valves can be switched between positions A and B. The solenoid valve is normally open and can be controlled via a simple button, to close and then re-open. Power to the valves is constantly on as soon as the control box is switched on. Upon shutdown of DickeBerta, the current valve positions are saved to a configuration file which is automatically loaded to pre-set the controls when the program is started.
- **MFC:** For the mass flow controller, the user enters a time period in seconds that defines how long the system is flushed with compressed air. A countdown starts in the background that shuts off the compressed air once the time has passed and the start button is reset.
- **Indicators:** Indicators inform the user of currently active digital output lines as well as motor positions, feedback lines and current state in the SPE procedure.
- **Error handling:** Should an error occur, information about the error is displayed on the user interface and a user dialog pops up requesting user interaction to determine if the program shall shut down.
- **Shutdown:** Shutdown of the program should always be initiated using the shutdown button in order to allow for saving of the relevant data and orderly exit from all processes.

Provided with these capabilities, the software was tested on the SCT eliminating any major bugs that inhibited smooth operation. After confirmation that all required functionality is provided for automated solid-phase extraction with the SCT, extensive laboratory testing was performed.

5.2.4 Laboratory Testing of the SCT-NMR Methodology

Extensive laboratory testing was initiated following the development of the semi-automated prototype, the SCT, and DickeBerta to control the SPE steps via a computer. Initially, the system was flushed with deionised water and the NMR solvent, 1 % CHCl_3 in PCE, to confirm that no contamination is present in the tubing, valves or cartridges. Subsequently, the stainless steel SPE cartridges were filled with 800 mg each of the Prevail C18 bulk sorbent material. Contaminated water samples were prepared by homogenising crude oil in deionised water and subsequent equilibration overnight. Two independent samples A and B were made up at different oil content to test the SCT over a wider range of concentrations. In order to confirm the initial tests on sample A, a manual SPE-NMR procedure was performed in parallel. Figure 5.13 shows the oil-in-water concentrations as determined for the two samples.

Figure 5.13 Oil concentration in two contaminated water samples (a) A and (b) B measured with automated SPE using the SCT and subsequent NMR measurement. Sample A was also measured once with the manual SPE-NMR procedure for validation purposes.

As can be seen from Figure 5.13a, agreement between manual SPE-NMR and semi-automated SPE-NMR (SCT-NMR) is excellent. The oil content as determined via SCT-NMR measurements shows some fluctuation over the duration of the experiments. This can be attributed to non-uniform distribution of the oil in the aqueous phase, loss of contaminant from the aqueous phase through evaporation over the course of the measurements and a continuously decreasing sample volume. SCT-NMR measurements of sample B, which was prepared at a higher oil content, exhibit a higher consistency across the five repetitions (refer to Figure 5.13b). This can be explained with the longer

5.2 Prototype Development and Construction

equilibration time between sample preparation and measurement for sample B compared to sample A which resulted in a more stable and consistent oil concentration in the aqueous phase.

In order to extend the laboratory tests to investigate the robustness of the SCT to a more aggressive bulk aqueous phase, a brine solution was prepared with the composition given in Table 5.3.

Table 5.3 Composition of artificial brine formulated by dissolving the respective salts in di-water.

Substance	Concentration [mg/L]
Ca	125
Mg	26
Fe	2
Na	3480
K	1000
Sr	15
Ba	28
Cl	5008
SO ₄	108
HCO ₃	1303
CH ₃ COO	1259
MEG	84

Two contaminated water samples C and D were then prepared by adding crude oil to the brine solution. With the intention to test the repeatability of the measurements and robustness of the system under extended operation, a 12-hour laboratory trial was conducted using samples C and D. Six SPE procedures were performed with each sample, the residual water was then measured with LLE-NMR for validation purposes. The concentrations of oil in samples C and D as obtained with SCT-NMR as well as LLE-NMR measurements are demonstrated in Figure 5.14.

Figure 5.14 shows a visible downward trend of oil concentration over time for sample C, whereas the oil content in sample D seems more consistent over time but comparatively lower on average. Some loss of contaminant through evaporation is expected. Given that sample D was deployed later than sample C but prepared at the same time, the lower and more consistent oil concentration is attributed to a longer equilibration time. A significant discrepancy between the LLE-NMR and SCT-NMR results was observed. The significantly larger measurement yield via LLE-NMR analysis can be explained with the sample composition. The oil content in the aqueous bulk sample will gradually migrate upwards due to its lower density compared to the brine, accumulate at the water surface and consequently, a concentration gradient develops. When using the SCT for the SPE procedure, the contaminated water is pumped out from the bottom of the sample bottle to load the cartridges. Therefore, the sample that remains after SCT-NMR measurements are concluded is

Figure 5.14 12-hour test of the SCT measuring oil content in contaminated water samples C and D via automated SPE and subsequent NMR analysis. Validation of the SCT-NMR measurements was performed with LLE-NMR on each sample.

composed mainly of the fraction close to the water surface and thus is expected to have a higher oil content. For the LLE-NMR measurements presented in Figure 5.14 above, this portion of the sample with elevated oil concentration, was used to determine the oil-in-water content. Additionally, the MEG and acid content of the brine possibly contributes to the LLE-NMR measurements. Due to their polar nature, these components are not extracted from the aqueous phase during SPE but are expected to transfer, at least to some extent, to the organic solvent during LLE.

As part of the development of an automated apparatus for quantitative SPE-NMR measurement of produced water, a field trial was anticipated with the semi-automated prototype (details of the field trial are provided in Section 6.4). The 12-hour test was the final check to prove that continuous operation is possible without failure and consistent results can be achieved.

During the laboratory testing of the SCT in a semi-automated setup (hence without in-line NMR measurement), a few issues with the selected components and setup were discovered. The three-way valves are easy to operate and perform according to their specifications. However, the orifices of the valves are big compared to the tubing size (1/4" ports for the valves) introducing a volume into the flow path that cannot be cleanly swept. Their L-port configuration (refer to the schematic in Figure B.10 in Appendix B) induces some carry-over when a valve is switched from one position to the other. The variation in tubing size — between 1/4" and 1/8" — and associated reducing unions also introduce dead volumes where fluid accumulates and cannot be swept entirely with the compressed air flush. Furthermore, the compressed air is not able to reach the tubing connecting valve 1 and 2 (see the PFD in Figure 5.6) thus generating mixing of the solvent and aqueous phase if not removed

Figure 5.15 PFD of the SPE and NMR analysis procedure as implemented with the semi-automated prototype. Highlighted are the problematic points in the setup. MFC = mass flow controller, V1 - V6 = electrically actuated ball valves, P1 and P2 = piston pumps for solvent and sample, respectively. Note that valve 6 is not used when performing the NMR measurement manually.

through an additional step when transitioning between the steps in the SPE procedure. Figure 5.15 shows the original PFD as adapted for semi-automated measurements, where the extraction sample is manually measured with the NMR spectrometer and the solvent is not recycled back into the supply vessel. Figure 5.15 also highlights the critical points in the system setup, such as the tubing between valves 1 and 2 (in red), the reducing unions to join different size tubing and the adapters required to connect 1/8" tubing to the 1/4" BSP inlets/outlets of the ball valves.

The SCT apparatus has been designed to fulfil the requirements for a subsea device in terms of pressure compatibility and power supply as well as automation as closely as possible. It is recommended, however, to deploy more advanced components in a further developed prototype to optimise the process flow, minimise any dead volumes and increase the compatibility with field requirements. For laboratory proof of concept testing and onshore field-trialling, the setup presented here was considered suitable.

5.3 Full Automation of the SPE-NMR Approach

The semi-automated version of the SCT was designed with prerequisites for incorporation of the NMR spectrometer to provide an in-line NMR measurement. Developing the semi-automated SCT

into a fully automated prototype consisted of connecting the NMR spectrometer to the flow path of the SCT and implementation of a remote control of the same, addition of a two-way solenoid valve as well as an extension of the LabVIEW program. These individual steps are described in more detail in Section 5.3.1.

5.3.1 Implementation of In-line NMR Measurements

The Spinsolve NMR spectrometer is equipped with a sample bore that is open from top to bottom. The minimum i.d. (inside diameter) is 5 mm in the sensitive region of the magnetic field. With respect to in-line NMR measurements, suitable tubing needs to give no interference with the magnetic field, show no proton resonance and have maximum inside diameter while maintaining an appropriate pressure rating. The latter is specifically important for the application to produced water analysis given the ppm level of the hydrocarbon analysis and the required sensitivity to perform accurate quantification. PEEK (PolyEther Ether Ketone), a thermoelastic polymer, is considered the best option for a tubing material as it is chemical resistant and has a high mechanical stability. It is predominantly applied for gas chromatography with common tubing sizes from 1/32" to 1/16" (outer diameter); PEEK tubing is not readily available at 3/16" or 5 mm outer diameter with an inside diameter of 1/8" or larger. Consequently, it was decided to choose FEP (Fluorinated Ethylene Propylene) tubing as an intermediate option despite its considerably lower pressure rating. With an o.d. (outside diameter) of 3/16" (4.76 mm) and an i.d. of 1/8" (3.18 mm), the selected tubing has a pressure rating of 41 bar. This is considered sufficient for preliminary laboratory testing and can be replaced by suitable PEEK tubing at a later stage.

The FEP tubing was connected to the stainless steel tubing (1/8" o.d.) with standard Swagelok reducing unions, on the FEP tubing side the stainless steel ferrules were replaced with PTFE (Polytetrafluoroethylene) to reduce the impact on the plastic. The flow path was complemented with a two-way solenoid valve, normally open, at the exit of the Spinsolve. This valve provides shut-off during measurement in order to keep the fluid stationary inside the magnet. The modifications to the setup are illustrated in the flow diagram in Figure 5.16.

The Spinsolve is typically shimmed with a sample of 90 % D_2O /10 % H_2O , with which a peak width at half height $LW_{1/2}$ of < 0.5 Hz can be achieved. With the setup as an in-line measurement, the shim sample cannot be used any more and instead, the water that exits from the SPE cartridges during solid-phase extraction is flown through the NMR spectrometer and deployed for shimming. Due to the decreased sensitive volume — the FEP tube has an i.d. of 3.18 mm compared to 4.16 mm of standard NMR tubes —, the attainable resolution is slightly impaired. Under operating conditions with the SCT running, a value of $LW_{1/2}$ between 1 and 1.5 Hz can be achieved. This is sufficient considering the objective of measuring oil in the extraction solvent at ppm level concentrations. A typical 1H NMR spectrum of the solvent mixture 1 % $CHCl_3$ in PCE obtained through in-line measurement with the Spinsolve is shown in Figure 5.17.

Figure 5.16 PFD of the SPE and NMR analysis procedure setup to provide a fully automated prototype. Highlighted are the modifications made to the original design. MFC = mass flow controller, V1 - V6 = electrically actuated ball valves, P1 and P2 = piston pumps for solvent and sample, respectively, NO = normally open, FEP = Fluorinated ethylene propylene.

Figure 5.17 ^1H NMR spectrum of the extraction solvent 1% v/v CHCl_3 in PCE measured with the Spinsolve NMR spectrometer in-line the SCT flow path. The CHCl_3 resonance (peak 1) is visible at $\delta \approx 7.26$ ppm along with a contaminant peak (peak 2) at $\delta \approx 1.2$ ppm corresponding to roughly 300 mg/L oil in the solvent.

Prior to measuring the spectrum shown in Figure 5.17, the magnet was shimmed to $LW_{1/2} = 1.12$ Hz. The pulse-and-collect sequence was then performed with a repetition time of 15 seconds averaging over 8 scans resulting in a total acquisition time of 2 minutes. The contamination peak visible in the spectrum at approximately $\delta = 1.2$ ppm is a degradation product from the solvent mixture itself as it had been exposed to UV light and oxygen before application. The CHCl_3 resonance at a chemical shift of approximately 7.26 ppm has a SNR value of 157, the SNR of the contamination peak at around 1.2 ppm is 16. The guideline for "Validation of analytical procedures: text and methodology" published within the context of the International Conference on Harmonisation [221], defines the limit of quantification (LOQ) at a SNR of 10:1. Thus the resolution is appropriate for quantification measurements of oil-in-water. To increase the sensitivity, additional averaging can be performed; this, however, comes at the cost of extended measurement time.

A potential option to increase the sensitivity NMR measurement is the alternative use of a CPMG echo train. As opposed to additional signal averaging, this would not significantly increase the experimental time. For this to be applied, the different T_2 values would need to be assessed to determine if an echo train can be quantitatively applied (need to be sufficiently long) and hence to define a suitable echo time. T_2 relaxation effects during the echo train will affect the ability to perform accurate quantification with the obtained spectrum and will need to be carefully assessed. T_1 relaxation between signal excitations would be the same for both FID and CPMG measurement protocols.

5.3.2 Remote Control and Automated Data Processing

In order to control the solenoid valve and the Spinsolve and perform automated post-processing as well as analysis of the resulting NMR spectra, the LabVIEW program was extended.

The Spinsolve supports remote control by means of a TCP-IP server which can handle multiple clients. The communication between the server and clients is enabled with text based XML messages. A set of Python scripts (these can be found in Appendix C) were developed that send and receive XML messages to start and stop (abort) NMR measurements as well as the shimming of the magnet. Within the LabVIEW program, the state machine main loop is extended to facilitate execution of the Python scripts and thus remote control of the Spinsolve. Once a NMR measurement or shim is completed, DickeBerta receives the last message from the Spinsolve and extracts relevant information for the user to be displayed on the user interface. After a NMR spectrum has been obtained, the user is asked for details about the measurement and sample which is logged into a text file for basic tracking. One log is created for each day and the content is amended after each NMR measurement.

In order to automatically process and analyse the spectra obtained through measurement with the Spinsolve, a Matlab algorithm was developed. The algorithm facilitates reading of the Spinsolve data files, FFT of the time domain data, baseline correction, phasing and conversion of the frequency scale

5.3 Full Automation of the SPE-NMR Approach

(x-axis) to chemical shift. Baseline correction is performed according to Golotvin and Williams [222]. In a first step, the baseline points are identified and extracted from the complete set of spectral points. A line is fitted through the baseline points and subsequently subtracted from the original spectrum. The baseline correction is combined with a phasing algorithm [223] that initially minimises an objective function based on the height difference of the peak tail ends. This is the so-called "coarse-tuning". A "fine-tuning" step follows that uses a negative penalty function to avoid negative peak points in the spectrum and thereby determines the exact phasing parameters. The concentration of oil-in-water can be derived from the post-processed frequency domain spectrum using fixed chemical shift ranges to define the integral areas for the reference and hydrocarbon resonances. On the LabVIEW user interface, the user provides the required input, i.e. sample and solvent volume, oil density and, if applicable, loads the data file with the baseline measurement (solvent recycling). To perform the data analysis, LabVIEW runs Matlab in the background executing the algorithm with the input data provided. Consequently, the output — oil concentration in the sample — is passed back to LabVIEW and subsequently displayed on the user interface. In the case of reusing the solvent and consequently measuring a baseline spectrum before eluting the SPE cartridge, the LabVIEW program automatically subtracts the baseline. The reader is referred to Appendix D for the Matlab script and relevant functions called therein.

On the user interface (front panel) of the LabVIEW program DickeBerta, two tabs were added to allow the user to control the measurements to be run with the Spinsolve (Figure 5.18a) and, once a spectrum is obtained, initiate the automated data processing and analysis (Figure 5.18b).

Figure 5.18 (a) NMR measurement and (b) data analysis tab on the GUI of DickeBerta to enable remote control of the Spinsolve and automated data processing of the measured spectra.

5.3.3 Initial Testing

Set-up of the SCT for fully automated SPE-NMR analysis and verification that the added system components respond to the LabVIEW program was followed by some basic tests. More comprehensive testing that involves a variety of contaminated water samples and validation measurements with alternative methods is the subject of Section 6.5.

After placing the NMR spectrometer next to the SCT and setting it up for the in-line measurements, the magnet had to be adequately shimmed. Deionised water was pumped into the FEP tubing and subsequently a so-called Powershim (shimming procedure provided by the Spinsolve software) initiated with the LabVIEW program. This automatic shimming procedure typically takes 45 min and, with the flow-through setup, can achieve a $LW_{1/2}$ value of around 1 Hz. After a Powershim has been performed once, a quicker shimming procedure — Quickshim — is used to optimise the magnetic field homogeneity. Note that the Spinsolve software is tuned to perform shimming with a 90 % D_2O /10 % H_2O sample in a standard NMR tube. Several Quickshims are usually required to achieve a linewidth $LW_{1/2} < 2$ Hz. According to the Spinsolve system, this value must be ≤ 1 for the system to be ready. However, as was shown above (Section 5.3.1, Figure 5.17), sufficient sensitivity is achieved with $1 \text{ Hz} < LW_{1/2} < 2 \text{ Hz}$ for the purpose of oil-in-water analysis.

Shimming the magnet was followed by rinsing the tubing, valves and an empty SPE cartridge with deionised water at 5 ml/min for around 30 minutes total. Compressed air was applied to clear the water from the system. Subsequently, the NMR solvent, 1 % $CHCl_3$ in PCE, was pumped through to remove any residual hydrocarbon or other organic contamination. The solvent was also used to verify that the sensitivity of the in-line NMR measurement is sufficient (see above) and to determine the optimum measurement parameters. For the standard NMR pulse-and-collect sequence, the following acquisition parameters have been established in the context of the automated SPE-NMR methodology:

- Number of scans: 8
- Acquisition time: 6.4 seconds
- Repetition time: 15 seconds
- Pulse angle: 90 degrees

These parameters are passed to the Spinsolve software via an XML message and subsequently, the measurement protocol 1D EXTENDED+ is initiated. The acquisition time determines the number of points as well as the dwell time for the experiment. A value of 6.4 seconds gives 32768 acquired points and a dwell time of 200 μs , thus the resulting spectrum has a chemical shift range of 63 to -54 ppm. The user can choose the number of scans on the user interface of DickeBerta, whereas the remaining acquisition parameters are preset in the relevant Python script for reasons of simplicity. As

can be seen in Figure 5.17 above, the chosen parameters provide adequate resolution and sensitivity for quantification purposes.

Following the initial flushing of the system and preliminary testing of the in-line NMR measurement, experiments were initiated to develop a suitable measurement protocol (see Section 5.3.4 below) and test the ability of the fully automated prototype to determine the hydrocarbon content of a variety of samples. Details of the experiments and discussion of the results is subject of Section 6.5 in the next chapter.

5.3.4 Protocol for Automated SCT-NMR Measurements

Preliminary measurements using samples of crude oil dissolved in deionised water were carried out to establish a consistent procedure for oil-in-water analysis with the advanced (fully automated) SCT-NMR prototype, hereafter referred to as auto-SCT-NMR. There are two options for the application in the laboratory: without and with solvent recycling. The former involves the disposal of the solvent extract after NMR measurement. In the case of solvent recycling, any solvent that was used for elution and measurement is transferred back into the solvent supply. For subsequent SPE procedures, NMR measurements need to be conducted to determine the build-up of contaminant in the solvent supply. A short breakdown of the steps required to perform auto-SCT-NMR measurement without and with solvent recycling is provided below. The steps are implemented with the LabVIEW program DickeBerta. A more comprehensive standard operating procedure is available (for reasons of comprehensibility, this is not included in this doctoral thesis) to guide the user during operation of the fully automated prototype.

Auto-SCT-NMR without Solvent Recycling

1. Select SPE cartridge and establish connection (if applicable).
2. Switch valves to correct position for loading.
3. Set loading volume and initiate the sample pump.
4. Shim the NMR spectrometer using the water that exits the SPE cartridge as the shim sample.
5. Switch valves to position for elution once the desired loading volume was applied (sample pump stopped).
6. Set elution volume and start solvent pump.
7. Monitor pressure and pumping volume; stop solvent pump when the solvent reaches the top of the tubing that is located inside the NMR magnet bore.

8. Obtain NMR spectrum (two-way solenoid valve closed during the measurement).
9. Pump additional 2 ml and obtain second spectrum. Repeat this x 1.
10. Analyse the spectra using the automatic processing implemented in DickeBerta.
11. Switch valves to position for compressed air flush and apply compressed air to remove solvent from the system.
12. Collect solvent that is flushed and discharge.
13. Return to step 1 and start the next measurement.

Implementation of solvent recycling in the auto-SCT-NMR methodology requires the addition of a baseline NMR measurement to determine the initial contamination in the solvent before the elution step is carried out

Auto-SCT-NMR with Solvent Recycling

1. Select SPE cartridge and establish connection (if applicable).
2. Switch valves to correct position for loading.
3. Set loading volume and initiate the sample pump.
4. Shim the NMR spectrometer using the water that exits the SPE cartridge as the shim sample.
5. Switch valves to position for compressed air flush once the desired loading volume has been applied; flush water from the system (into aqueous waste container).
6. Switch valves to position for baseline measurement and initiate solvent pump to fill NMR spectrometer with solvent.
7. Obtain NMR measurement of solvent (prior to elution).
8. Switch valves to position for compressed air flush and flush the solvent from the system (feed back into the solvent supply container).
9. Switch valves to position for elution.
10. Set elution volume and start solvent pump.
11. Monitor pressure and pumping volume; stop solvent pump when the solvent reaches the top of the tubing that is located inside the NMR magnet bore.
12. Obtain NMR spectrum (two-way solenoid valve closed during the measurement).

13. Pump additional 2 ml and obtain second spectrum. Repeat this x 1.
14. Analyse the spectra using the automatic processing implemented in DickeBerta including the associated baseline measurement.
15. Switch valves to position for compressed air flush and apply compressed air to remove solvent from the system.
16. Feed solvent back into the solvent supply container either manually or directly via connected tubing.
17. Return to step 1 and start the next measurement.

Note that the procedures are based on a user operating the LabVIEW program. At this stage, the program requires user input to perform the individual steps. The setup is yet to be optimised to enhance performance and allow fully autonomous operation.

5.4 Conclusion

A fully automated prototype to facilitate SPE in combination with in-line NMR measurements to analyse the oil content in produced water was built. Initially, the SPE-NMR approach was carried out manually using a simple setup with a peristaltic pump, commercially available SPE cartridges and manual NMR analysis. This methodology was advanced and developed into an automated apparatus with the objective to be deployed as a laboratory and onshore field device. Technical requirements for a produced water discharge sensor were defined with the sensor's main function of the quantitative analysis of the oil content for regulatory compliance monitoring. A suitable sensor should require minimal maintenance and operate autonomously and reliably for an extended period of time (e.g. 5 years).

Initially, an apparatus designed for supercritical fluid extraction (high pressure) was re-purposed and deployed for automated solid-phase extraction. Consequently, this apparatus served as a model for the design of a novel device that implements SPE and subsequent NMR analysis. A mobile sampling device, the self-contained transportable (SCT), that accommodates the SPE cartridges, pumps, valves, containers for the sample, solvent and waste, a mass-flow controller, tubing and the necessary electronics was built. The individual components were selected according to the specific requirements associated with long-term and in field application. Selection criteria regarding control and power supply feasibility, commercial availability and the objective of building a prototype for bench-scale testing in the laboratory and in the field onshore were taken into account. The deployed components and current setup are not capable of being applied subsea and ample scope is given with respect to the selection of superior components.

The SCT is controlled with a laptop and a LabVIEW program, DickeBerta, enabling operation of the individual components and thus execution of the SPE automatically. At first, the extracted sample was measured manually with the NMR spectrometer to allow troubleshooting of the SCT and software. The robustness of the device was tested both in the laboratory and in the field. Validation against alternative methods was performed in an intermediate step (see Chapter 6 for a comprehensive description) before advancing the prototype to full automation.

The fully automated, working prototype includes the NMR spectrometer as part of the SCT flow path. Both the sample and the solvent can be directed through the NMR bore either directly from the supply containers or after passing through a SPE cartridge. Inside the NMR spectrometer, FEP tubing is deployed as a non-magnetic, non-protonated material to direct the sample into the sensitive volume. The acquisition of a NMR spectrum is initiated on the stationary sample (shut-off valve at tube exiting the magnet) using an extended version of the LabVIEW program. Post-processing as well as data analysis to extract the oil-in-water concentration from the obtained spectrum is also executed automatically with the help of a Matlab algorithm. Preliminary testing of the advanced prototype confirmed its ability to implement the SPE-NMR approach. Thereupon, extensive laboratory testing using contaminated water samples was required in order to establish a suitable measurement protocol. Validation and verification of the results obtained via auto-SCT-NMR measurements against alternative methods is described in the following chapter.

Chapter 6

Robustness of SPE-NMR Analysis for Produced Water

Oil-in-water analysers for compliance monitoring in the oil and gas industry have to yield reliable and accurate results despite fluctuating levels of oil concentration as well as varying oil and bulk sample (brine) compositions. Once installed either onshore, offshore or subsea, maintenance on the sensor must be minimised and, ideally, only required at planned intervals. In this context, the robustness of the SPE-NMR approach for quantitative produced water analysis and the viability of the developed prototype under field conditions is investigated.

Section 6.1 describes the tests regarding the performance of the selected sorbent material when reused for multiple solid-phase extractions. The intention here is to show that a limited number of SPE cartridges can be used to design a sensor that can operate autonomously for an extended time period. On that account, NMR solvent recycling and reuse is scrutinized in Section 6.2. These studies are followed by extensive testing of the semi-automated prototype for the analysis of field samples both in the laboratory (Section 6.3) and during a field trial at an onshore gas plant (Section 6.4). Lastly, Section 6.5 describes the testing and validation of oil-in-water measurements with the fully automated SPE-NMR prototype in the laboratory. A brief summary and conclusion follows in Section 6.6.

6.1 Recyclability of the SPE Cartridges

Significant for the application of the SPE-NMR methodology for oil-in-water monitoring at remote locations is the recyclability of the SPE cartridges or more specifically the sorbent material.

Ultimately, the automated SPE-NMR sensor needs to operate autonomously for an extended period of time without manual intervention. The supply of SPE cartridges will necessarily be limited as well as

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the allocated space restricted. Therefore, the SPE cartridges that are installed have to be reused and applied for multiple measurements.

The reusability of two Prevail C18 cartridges was assessed over a period of two and a half months with ten independent samples A to J of water contaminated with crude oil. The samples were prepared by adding approximately 2 ml of a locally sourced, aliphatic crude oil to 2 L of deionised water and homogenising the two phases at 10500 rpm for 1 min. The samples were left overnight to equilibrate before analysing the dissolved oil with the SPE-NMR methodology. To start with, only one cartridge, "#1" was used for the measurements. Cartridge "#2" was introduced later in order to examine the performance of the sorbent material at different stages of recycling. Cartridge "#1" was used 30 and "#2" 20 times in total. The idle time between measurements varied randomly and no treatment was applied between or before measurements (i.e. no conditioning or wetting of the sorbent material). For ease of visual observation of the sorbent material, the commercially available Prevail C18 were used in the manual SPE procedure as outlined for the proof-of-concept measurements (for details refer to Chapter 3). The conditions for the SPE procedure were consistent across all measurements: 150 ml loading volume and 10 ml elution at a flow rate of 5 ml/min. The two cartridges were reused two to five times on one sample and typically run concurrently. Further to the reused cartridge, one fresh Prevail C18 cartridge was used for each sample as a validation measurement. Figure 6.1 shows oil-in-water concentrations of three independent samples resulting from SPE-NMR with reused cartridges. Note that for reasons of clarity and comprehensibility, only a selection of measurements is displayed.

Figure 6.1 Concentration of total OiW for contaminated water samples determined with SPE-NMR. Two Prevail C18 cartridges were reused multiple times on three independent samples. Shown are the results for recycles 9 to 18 and 21 to 30 of cartridges # 1 and # 2, respectively, as individual measurements of samples H, I and J.

6.1 Recyclability of the SPE Cartridges

Figure 6.1 shows the individual measurements with each cartridge on the three independent samples along with the reference measurements conducted using a fresh Prevail C18 cartridge. A divergence between the fresh Prevail C18 and the reused cartridges is evident for sample H, samples I and J show excellent agreement. The individual measurement on each sample can be summarised to give an average oil concentration; this is presented in Figure 6.2 below.

Figure 6.2 Average concentration of total OiW of three independent contaminated water samples H, I and J as determined with SPE-NMR deploying two reused Prevail C18 cartridges. Error bars represent the standard deviation across the repeated measurements with the same cartridge on the each sample.

The calculated averages for the three samples, shown in Figure 6.2, are consistent but exhibit significant standard deviations. These are, however, comparable for the two cartridges. The large fluctuations across the repeated measurements on each sample can be explained by the experimental setup and procedure. Typically, a concentration gradient develops in the water sample as the oil migrates towards the sample surface over time. The SPE cartridges are loaded from the bottom of the sample, thus as the experiment progresses, the water level drops. Consequently, the measured oil content is expected to increase with progressing number of SPE-NMR measurements for the same sample. This trend is clearly visible for sample I, which was measured five times with each cartridge (Figure 6.1). With only three and two measurements for samples H and J, respectively, the water level would not have dropped sufficiently for the concentration gradient to be mirrored in these results. The reference data points determined through SPE-NMR analysis with fresh Prevail C18 cartridges confirm that the cartridges have not degraded after being reused for 30 times and are still capable of generating reliable OiW measurements.

Using the thus far established maximum recycles of 30 with one SPE cartridge, scale-up calculations can be performed in consideration of a SPE-NMR device for field application. If a total

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of five measurements are taken per day over a period of three years, a total of 183 cartridges are needed (each one recycled for 30 times). However, during the recycling experiments, no evidence of degradation was observed leading to the assumption that more than 30 recycles are possible. Table 6.1 below summarises the scale-up conditions and amount of SPE cartridges needed for different cases.

Table 6.1 Scale-up of SPE cartridges for field application for different cases of maximum recycles per cartridge.

SPE per day	Lifetime [years]	Max. recycles per cartridge	No. of cartridges needed
5	5	30	305
		50	110
		100	55

Option three is the most feasible with just over 55 SPE cartridges required to achieve a lifetime of three years. The hypothesis that the cartridges can be reused for 100 SPE procedures has to be corroborated in the future.

6.2 Solvent Recycling

Similar to the cartridges, the solvent must be reused in order to extend the lifetime of an apparatus with limited solvent supply. The necessary solvent recycling consists of feeding the solvent back into the supply container after elution of the SPE cartridges and NMR measurement. Consequently, the oil contamination in the solvent will build up as more SPE-NMR measurements are performed. In order to account for this increasing concentration, a baseline NMR spectrum is obtained before the SPE elution which is subsequently subtracted from the measurement of the actual elution extract. Thus, to yield the oil content in a produced water sample, two NMR analyses are required — before SPE to establish the base contamination and after SPE to determine the amount of oil added to the solvent.

Initial tests of solvent recycling were conducted using the manual laboratory setup with the peristaltic pump and the 900 mg Prevail C18 SPE cartridges (refer to Section 3.3 for a detailed description). A volume of 500 ml NMR solvent, 1 % CHCl_3 in PCE, was prepared and used as the solvent supply for the SPE-NMR measurements. After each SPE procedure and NMR analysis, the used solvent was fed back into the supply bottle and mixed thoroughly with the stock solution. Before the elution step of the next SPE, a sample of the solvent was measured with the NMR spectrometer to establish the current baseline. The increasing oil content in the solvent was monitored over time and plotted versus the number of reuses as can be seen in Figure 6.3 below.

Figure 6.3 shows a rapidly and almost linearly rising oil concentration in the solvent. Minor inconsistencies in the linearity are observed. These can be partly explained by the experimental procedure which included several sets of experiments. The sets were separated by considerable time

Figure 6.3 Concentration of oil in the NMR solvent system (1 % CHCl_3 in PCE) as a function of solvent reuses. The dashed lines separate the individual measurement sets. One use is defined as elution of a SPE cartridge with 10 ml of solvent. The dashed lines separate the individual measurement sets.

intervals, 12 hours to several days, during which the solvent reached a potentially different equilibrium state. Furthermore, for each experimental set, the rate of increase in oil content is dependent on the water sample and variabilities in sample concentrations. Thus changes in the slope are visible within the same set of experiments.

Experimental conditions were chosen to induce accelerated ageing by using contaminated water samples with a considerably high oil content at 50 to 100 mg/L in water. This is reflected in the steep slope of the curve reaching 1500 mg/L after 65 uses of the solvent. As the oil content increases beyond 1500 mg/L in the solvent, the results obtained through SPE-NMR measurement started to show discrepancies, in particular with respect to samples of lower oil concentration. A maximum of 1500 mg/L oil in the NMR solvent was established while still yielding consistent results that did not deviate in accuracy relative to lower concentrations. This value will need to be further refined as part of future work.

A scale-up regarding the solvent can be done to establish conditions for the deployment of a SPE-NMR device in the field. Given a solvent supply of 30 L, a lifetime of just over five years can be achieved. The relevant conditions and scale-up values are presented in Table 6.2.

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Table 6.2 Scale-up of the solvent supply for field application of a SPE-NMR device given a maximum oil concentration in the solvent of 1500 mg/L and assuming a load volume of 150 mL for each SPE.

Solvent supply [L]	Maximum OiW [mg/L]	SPE per day	Oil mass added per SPE [mg]	Lifetime [years]
30	30	5	4.5	5.4

The initial testing of reusing the SPE cartridges as well as recycling the solvent demonstrated the capability of the (manual) SPE-NMR measurement approach to be further developed for industry application. The recycling tests are resumed with the semi- and fully automated prototype both with artificial as well as field samples of produced water as described in the following sections 6.3, 6.4 and 6.5.

6.3 Field Samples

To begin with, measurements using the SPE-NMR approach were conducted on artificial produced water samples that consisted of a locally sourced crude oil dissolved in deionised water. Compared to field samples of produced water, these artificial samples are less complex regarding the sample composition, do not contain any unknown contaminants and can be prepared to cover a wide range of oil concentrations. In order to test the robustness of the SPE-NMR methodology, field samples need to be used. Typically, production chemicals are present in these samples, for example corrosion and hydrate inhibitors, in addition to dissolved and dispersed solids and they can have a high or variable salinity. This results in a more complex and generally unknown composition and potentially impacts oil-in-water measurements.

With the intention to investigate the ability of the SPE-NMR method implemented in the form of the semi-automated prototype (SCT-NMR), as described in Section 5.2, to accurately determine the oil content in produced water, field samples were sourced. For validation of the SCT-NMR results, liquid-liquid extraction in combination with IR-QCL (LLE-IR) and GC-FID (LLE-GC) was performed. In addition, LLE in combination with NMR (LLE-NMR) using the same solvent as for the SCT-NMR methodology, served as a fourth independent measurement.

6.3.1 Methodology

A total of 6 L of produced water from an onshore gas and condensate production facility in Western Australia's Northwest were obtained. The produced water was sampled into 1 L amber glass bottles from 2 different locations on the platform. Sample "A" was taken at the back end of the gas flotation vessel whereas sampling for sample "B" was done directly before overboard discharge of the

produced water. As no treatment is applied between the 2 sample locations, the samples were expected to give very similar results regarding the oil content. The samples were acidified to a pH 2 – 3 and stored in a fridge at 2 – 4 °C. On the day of measurement, one sample bottle was taken from the fridge and equilibrated to room temperature. Subsequently, measurements were started. The 1 L sample was divided into appropriate portions for the LLE-IR, LLE-NMR and SCT-NMR procedures.

The SCT-NMR method uses the semi-automated prototype (detailed description of the prototype development can be found in Chapter 5) to perform sample preparation with solid-phase extraction and manual, quantitative NMR analysis of the obtained solvent extract. For the SPE procedure, the loading is performed with a sample volume chosen to not exceed the sorbent's retention capacity and to conform to the detection requirement of the low-field NMR spectrometer. The loading volume was 150 or 200 ml; increasing the load volume to 200 ml was regularly done to confirm that sufficient pre-concentration can be achieved with 150 ml. After loading, air flushing with compressed air at 25 bar was carried out to remove residual water from the sorbent. Elution was then performed with the NMR solvent mixture of 1 % v/v CHCl_3 in PCE. The minimum elution volume realised was 10 ml (previously shown to be sufficient for maximum recovery of the retained hydrocarbons from the sorbent, refer to Section 3.10 and Figure 3.18), the exact volume varied between measurements. The elution volume along with the loading volume was noted for each SPE to determine the pre-concentration factor. A portion of the solvent extract was ultimately transferred into an NMR tube (approximately 1 – 2 ml) and measured in the NMR spectrometer. The resulting spectrum was post-processed and analysed to determine the oil content in the solvent and consequently infer the oil-in-water concentration of the measured sample. Typically, four SCT-NMR measurements were conducted on each of the six samples. Both fresh SPE cartridges and reused cartridges were deployed for the measurements.

LLE in combination with NMR analysis was performed to provide an independent measurement using the same solvent (1 % v/v CHCl_3 in PCE) but without extraction over a solid sorbent material. One measurement was conducted at the beginning of the day in parallel with the first SCT-NMR measurement and the LLE-IR procedure. The subsequent NMR analysis of the solvent extract was conducted in the same manner as during the SCT-NMR measurements.

The methodology for the LLE-IR measurements was adopted from general industry practice as commonly applied in Western Australia. This consists of Total Oil and Grease (OG) measurements, where the hydrocarbon content extractable with a solvent in a liquid-liquid extraction procedure is determined. The obtained solvent extract is further passed through sodium sulfate to remove any residual water before the measurement. For the purpose of Total Petroleum Hydrocarbon (TPH) measurements, the OG extract was additionally filtered through silica gel (in the form of cartridges) to remove polar compounds. Typically, 3 extractions were performed on the same sample yielding 3 OG as well as 3 TPH solvent extracts, which were measured twice each with the IR instrument. GC-FID analysis was also conducted on the solvent extracts from the LLE-IR procedure. Approximately 2 x 2 ml each were taken from the OG and TPH samples and transferred into glass

vials. These were run in the GC-FID over night after LLE-IR, LLE-NMR and SCT-NMR measurements were completed for the day.

Prior to the analysis of the produced water samples, both the IR spectrometer and the GC-FID were calibrated with standard solutions of condensate in cyclohexane. Neat condensate was available that was sampled at the same time as the produced water from the production facility. Four calibration standards at 25, 50, 100 and 200 mg/L were formulated by dissolving the equivalent amount of condensate in the cyclohexane solvent and measured in triplicate with the IR spectrometer. The established calibration relating the oil concentration (y) to measured absolute absorbance (x) is given by:

$$y = 19.289x + 0.3126 \quad (6.1)$$

The coefficient of determination for the correlation in Equation 6.1 is $R^2 = 0.9997$.

The same calibration standards were used for calibration of the GC-FID. However, due to comparatively higher sensitivity of the instrument and the conceivable concentration range of the measurements, only three points (25, 50 and 100 mg/L) were included. The correlation between peak area (x) and oil concentration (y) was determined as follows:

$$y = 36.399x + 16.202 \quad (6.2)$$

The associated coefficient of determination was determined to be $R^2 = 0.9995$ and the effective (lower) detection limit corresponds to the offset, 16.202 mg/L, as provided by Equation 6.2.

For the analysis of the GC-FID chromatograms, the peaks were integrated between retention times of 7.9 min (chosen so that the solvent peak is discarded) and 22 min (the condensate does not present any components beyond a retention time of greater than 22 min).

6.3.2 Results and Discussion

The first notable visual observation was that the LLE procedure for NMR analysis generated water-in-solvent emulsions with samples B taken downstream, just before discharge. Samples A did not show this behaviour. Given enough time for phase separation (≥ 1 hour), the droplets eventually coalesced forming larger droplets and a portion of the solvent extract could be transferred to a NMR tube for measurement. The NMR measurement is robust with respect to slight water contamination and spectra were readily acquired. Emulsions were not observed during the LLE-IR procedure; this is attributed to differences in sample preparation where the LLE is performed in a separation funnel and the ratio of solvent to produced water sample is much higher. Furthermore, passing the solvent extract through sodium sulfate removes any water droplets that are contained in the solvent phase.

The first set of measurements was conducted on the first litre of samples A, referred to as sample A #1. Note that the sample was not equilibrated to room temperature before initiating the experiments

and it remained cold until cessation of the SCT-NMR measurements (the sample bottle was placed in a metal container that provided insulation throughout the duration of the measurements). The results of oil-in-water concentration in sample A #1 are shown in Figure 6.4. The OG and TPH results determined with IR and GC-FID are displayed in Figure 6.4a, whereas Figure 6.4b shows the LLE-NMR and SCT-NMR results. Noticeable is the very high reading of extract #1 with GC-FID in Figure 6.4a yielding 113 mg/L OG. Furthermore, subsequent extracts measure high OG results both with IR and GC-FID and the measurements do not drop to a reasonable level of below 5 mg/L as would be expected. In comparison to the IR and GC-FID results, Figure 6.4b shows consistently lower measurements around 25 mg/L for the SCT- and LLE-NMR measurements.

Figure 6.4 Oil-in-water measurements of sample A #1 as (a) OG content from 3 extracts and 1 TPH extract determined with IR and GC-FID and (b) total oil content measured with SCT-NMR and LLE-NMR in 4 and 1 repeat(s), respectively.

Before proceeding to test the remaining produced water samples, the cause of the divergence across the applied methods was investigated. The chromatograms of one OG and one TPH extract were compared to the 25 mg/L calibration standard, as shown in Figure 6.5, to check for additional, unidentified peaks. Note that for reasons of comparability, only the second OG extract of sample A #1 is plotted (its peak amplitudes are lower) and the retention time limited to the range relevant for integration.

The chromatograms reveal contaminant peaks between 8 and 15 minutes that present a comparably high intensity in the OG extract and which do not appear in the TPH extracts. The chromatogram of the calibration standard indicates that these contamination peaks did not originate from the neat condensate itself. Through investigation of possible sources of contamination in the sample preparation and measurement procedure, it was established that the extraction procedure did not introduce any contamination into the measurement. Consequently, it was concluded that the peaks highlighted with asterisks in Figure 6.5 were not part of the "total oil content" and could be subtracted from the gas chromatograms to provide a potentially more reasonable OG result. It is assumed that the contaminant(s) originate from the production and / or water treatment process implemented on the

Figure 6.5 Chromatograms of OG (anthracite) and TPH (light grey) extracts from sample A #1 in cyclohexane and the original 25 mg/L condensate in cyclohexane calibration standard (black). Shown are the retention times relevant for determination of total integral peak area starting from 7.9 min as indicated with the dashed line. Asterisks mark the peaks that do not originate from the condensate.

facility where the samples were taken, however, no details in this respect were obtained from the facility operator.

A summary of the SCT-NMR and LLE-NMR measurements along with the OG and TPH extract #1 results determined with IR and GC-FID (contamination peaks omitted from the total integral peak area) from measurement set 1 (A #1) are shown in Figure 6.6.

The graph illustrates that the SCT-NMR agrees well with both LLE-NMR and the LLE-GC result for OG. The IR reads the highest result for OG and the lowest for TPH. For the second and third extraction according to the analysis with GC-FID, no residual OG was detected once the contaminant peaks were subtracted from the chromatograms.

As an example of results for samples B, Figure 6.7 shows SCT-NMR and LLE-NMR measurements compared to the OG and TPH extract #1 results as analysed with IR and GC-FID (again, the contamination peaks were not included in the total integral peak area) for sample B #3. Note that the OG measurement with LLE-IR is omitted due to its comparably high value.

Agreement between the two NMR methods is excellent; both LLE-GC results are broadly consistent with the SCT- and LLE-NMR readings. The LLE-IR measurement regarding TPH content is larger than all other results.

The rest of the produced water samples were then measured as outlined above subtracting the peaks considered contamination from the GC chromatograms. Figure 6.8 provides a summary of the

Figure 6.6 Oil-in-water concentrations for sample A #1 as determined with SCT-NMR, LLE-NMR, LLE-IR and -GC where the GC result is corrected for the contamination. For IR and GC-FID, OG and TPH results from the first extract are shown. These as well as the LLE-NMR results are displayed in line with SCT-NMR measurement 1 as the LLEs were carried out in parallel.

measurements on the 6 samples as determined with SCT-NMR, LLE-NMR as well as LLE-IR and -GC (OG and TPH).

Note that the GC-FID and IR results in Figure 6.8 are from the first extract only and do not present the accumulative value of multiple extractions. As reasoned above, the oil content determined with IR of the second and third extraction of the same sample did not drop to a reasonable level and was discarded for further interpretation. The GC-FID analysis on the other hand did not show any residual peaks in the chromatograms after the first extraction. Consequently, averages from individual measurements are only shown for the SCT-NMR measurements. These sit somewhere between the OG and TPH results from the first extract determined through LLE-GC analysis. Both the SCT-NMR and the GC-FID results are consistent with little variation across the different samples. The OG concentrations determined with IR are throughout considerably higher, whereas the TPH results are low for measurements 1 – 4 and then exhibit increasing values. The LLE-NMR results present two outliers, but show excellent agreement with the SCT-NMR on the remaining three samples.

In the SPE procedure as implemented with the semi-automated prototype (SCT-NMR), the hydrocarbon contamination is extracted from the aqueous phase through retention of the compounds via non-polar, hydrophobic interactions with the sorbent material. In this process, highly polar compounds are not retained. The SCT-NMR measurements thus correspond most to the TPH values. As demonstrated in Figure 6.8, the GC-FID-TPH and SCT-NMR results show reasonable agreement. On the same note, the GC-FID-OG results have to be interpreted with caution as the contaminant

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Figure 6.7 Oil-in-water concentrations for sample B #3 as determined with SCT-NMR, LLE-NMR, LLE-IR and -GC. For IR only the TPH result from extract 1 is shown. LLE-IR, LLE-GC and LLE-NMR results are displayed in line with SCT-NMR measurement #1 as the LLEs were carried out in parallel. The second LLE-NMR was performed on the remainder of the sample after the SCT-NMR measurements were completed.

peaks were subtracted manually without knowledge of the contaminant source. It is assumed that the resulting concentration is slightly higher than the true value due to the manual subtraction procedure and the possibility that additional contaminant peaks, albeit small, are still included when integrating the remaining peaks.

The results obtained from the SCT-NMR measurements with the semi-automated prototype were compared to LLE-NMR as well as LLE-GC and -IR measurements performed according to industry practice. The SCT-NMR results were consistent and confirmed the anticipated oil-in-water concentrations of below 30 mg/L. General agreement with the results obtained from GC-FID analysis was demonstrated. However, some contamination was present in the produced water samples that seemed of a polar nature and contributed considerably to the readings with the IR spectrometer. More detail about the sampling locations within the treatment process and added chemicals was not available to help interpret the findings. Unfortunately, such information was not available due to commercial sensitivity. In conclusion, the semi-automated prototype demonstrated its ability to yield reliable and consistent results regarding the oil content of field produced water samples and showed robustness to the greater complexity of the samples. Reusing the SPE cartridges did not show any adverse impact on the consistency of the results.

Figure 6.8 Average oil-in-water concentration for the six individual samples as determined with SCT-NMR, LLE-NMR and LLE-IR and -GC measurements. For both the IR and GC-FID, only the results from extraction 1 are shown. Error bars on the SCT-NMR results indicate the standard deviation across repeat measurements.

6.4 Field Trial with the Semi-Automated Prototype

Conducting a field trial formed an essential part in the development of the SPE-NMR prototype in order to test the components under field conditions and show the applicability of the methodology to real contaminated water. An opportunity was given by Woodside Energy Ltd. to use their Pluto LNG (liquefied natural gas) Plant near Karratha, Western Australia, for a two-week onshore trialling of the SCT and NMR measurements. The main objective of the field trial was the operation of the SCT and NMR spectrometer on site and validation of the SCT-NMR measurements against alternative methods. The robustness of the SCT was to be tested via prolonged exposure to elevated and fluctuating temperatures and humidity, dust, UV radiation and wind. Furthermore, it was anticipated to investigate the performance of the benchtop NMR spectrometer Spinsolve when exposed to plant equipment and unstable surrounding conditions.

6.4.1 Field Trial Set-up and Sampling

The key equipment to be trialled under field conditions were the SCT and the NMR spectrometer. Additionally, a benchtop infrared (IR) spectrometer — the Eracheck from eralytics GmbH, Austria — was to be applied to give an independent and alternative measurement to the ¹H NMR analysis. The equipment was disassembled for the transfer from Perth to Karratha (1530 km) and then re-assembled

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on site at Pluto LNG. All of the instruments and system components remained in working order after the transfer.

None of the equipment taken along for the field trial was classified as intrinsically safe and thus had to be located on site in a non-hazardous, green area of the plant. Operation of the SCT was allocated to a green road situated within the Effluent Treatment Plant (ETP) on Pluto LNG in close proximity to the Oily Water Equalisation Tanks (OWETs), this is shown in Figure 6.9a. A scaffold was put up to delimit the area assigned to the work permit for the research, provide some shade and storage space for the equipment. The SCT remained outside throughout the duration of the field trial exposed to the naturally fluctuating environmental conditions (i.e. temperature, humidity, dust and UV radiation). After the equipment was re-assembled, the functionality of the SCT and the analysis tools was verified with some preliminary tests. In total, the SCT was operated on site over eleven consecutive days and approximately ten to twelve hours per day. One night shift was conducted to extend the uninterrupted operating window to 36 hours and test the robustness with respect to larger temperature and humidity fluctuations.

The two analysis tools, the Eracheck (IR) and Spinsolve (NMR), were accommodated in an on site laboratory approximately 50 m away from the setup of the SCT within the ETP area. The lab was air-conditioned and protected the instruments from UV radiation. Chemicals, laboratory equipment and spares were also stored in the laboratory. The extraction samples of oil in the NMR solvent were transferred manually between the location of the SCT and the laboratory for analysis. During one dayshift in the second half of the field trial, the NMR spectrometer was relocated to the outside next to the SCT to investigate its ability to cope with elevated temperatures, UV radiation and plant equipment in near proximity.

Figure 6.9 Location of the sampling point for daily analyses of oil-in-water concentration. (a) Location of the scaffold and the SCT on the green road in the ETP, in proximity to OWET A and B. (b) OWET B. (c) Valve from which the daily samples were extracted near the bottom of OWET B.

6.4 Field Trial with the Semi-Automated Prototype

At the time of the field trial, only one of the two oily water tanks — OWET B — was on-line and available for sampling. The allocated sample point for the field trial samples was located near the bottom of OWET B (the tank has a capacity of 1700 m^3). Figures 6.9b and 6.9c show the tank and detail the location of the sample point on OWET B.

All contaminated, aqueous effluents from the Pluto production facility accumulate in the OWETs and are subsequently directed through the water treatment package before discharge. The effluents are a collection of Accidentally Oil Contaminated (AOC) and Continuously Oil Contaminated (COC) streams as well as the MEG Distillation Column overheads. Other discharge water streams, for example from cleaning activities in the facility, are also managed in the ETP. If the volume level in the OWETs drops below 30 %, water from the discharge tank — common discharge water, considered clean — is fed into the tank to raise the liquid level and dilute the content. Due to the inconsistent feed streams with differing compositions, the exact contents of the oily water cannot be known and will vary greatly. The presence of solids is also anticipated, specifically near the bottom where they accumulate due to gravity separation. Thus, the samples taken from OWET B are considered adequate to test the robustness of the SCT with respect to complex and varying sample composition as well as the presence of additional contaminants (i.e. production chemicals) and solids.

On average, samples were taken twice per day from OWET B (see Figure 6.10 for location of the sampling point within the ETP), typically once in the morning upon shift start and a second set taken around midday or early afternoon. Three samples were bottled at the same time, one sample of approximately 1000 mL was intended for the SCT and two additional samples of 150 or 200 mL were to be analysed with LLE-IR and LLE-NMR, respectively. As soon as the samples were taken, the SCT was started up. In parallel with the first SPE, LLE was carried out in the laboratory. Usually, 3 to 4 SPE procedures were conducted on the same sample and the leftover "old" sample subsequently replaced with a fresh oily water sample (second sampling). Any residual sample was analysed with LLE-NMR and, if enough volume was available, with LLE-IR.

In addition to the regular oily water samples from OWET B, two samples downstream of the OWETs were made available for testing (day 12 of the field trial). One sample was taken before and another one after the Membrane Bioreactor Package in the ETP. A schematic of the process flow in the ETP is shown in Figure 6.10 below with indication of the sampling locations.

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Figure 6.10 Simplified flow diagram of the general process steps in the ETP and the location of the sampling points during the field trial. MEG = Monoethylene Glycol, COC = Continuously Oil Contaminated, CDF = Controlled Discharge Facility, OWET = Oily Water Equalisation Tank, MBR = Membrane Bioreactor Package.

The intention here was to test the ability of SCT-NMR to capture lower oil-in-water concentrations. Table 6.3 summarises the number of measurements performed with each method over the duration of the field trial.

Table 6.3 Test matrix summarising the number of measurements performed and samples taken during the field trial. OWET = Oily Water Equalisation Tank, MBR = Membrane Bioreactor Package

Date	Sampling frequency per 12 hr shift	Sampling location(s)	SPE-NMR [#]	LLE-NMR [#]	LLE-IR [#]
29/09/2017	2	OWET B	3	3	1
30/09/2017	2	OWET B	7	4	2
01/10/2017	2	OWET B	5	3	0
02/10/2017	2	OWET B	7	4	2
03/10/2017	2	OWET B	6	4	1
03 - 04/10/2017	2	OWET B	7	4	1
04/10/2017	2	OWET B	5	4	0
05/10/2017	2	OWET B	5	3	3
06/10/2017	2	OWET B	6	3	3
07/10/2017	1	OWET B	4	2	1
08/10/2017	3	After MBR	2	1	1
		Before MBR	2	1	1
		OWET B	3	2	1
09/10/2017	1	OWET B	6	1	1
Total	23		68	38	19

6.4.2 Results and Discussion

This section provides a comprehensive summary and discussion of the measurements performed at Pluto LNG. Initially, the performance of the SCT and the NMR spectrometer is briefly outlined, which is followed by details regarding the oil-in-water analysis done with SCT-NMR, LLE-NMR and LLE-IR. Lastly, a comparison between the results obtained by the UWA research team with independent measurements conducted by an off-site, Woodside operated laboratory is presented.

Throughout the duration of the field trial, all components remained operational and no replacement was necessary. The electrical and moving components were not affected by the elevated temperatures and humidity, nor did dust have any impact on the working order of the equipment. In addition to hydrocarbon contamination, the contaminated water sampled from OWET B contained unknown amounts of various process chemicals as well as dissolved and suspended solids. Notably, the samples were taken from the bottom of the tank where the heavier components, for example solid particulates, will accumulate. Despite being visibly present and having an effect on the LLE procedure (development of water-in-oil emulsions), the additional components did not affect the SPE procedure or any component of the SCT. This can partially be attributed to the operating conditions as the maximum number of recycles with one cartridge was limited to nine in total and the capability in this respect not exhausted.

During the field trial, the NMR spectrometer was mainly operated in the on-site laboratory as the magnet is tuned to surrounding temperatures of 19.5 to 25.5 °C and can be affected if the temperature is not in the specified range. On day 13, the Spinsolve was transferred from the laboratory to be located outside next to the SCT under the scaffold. The intention here was to test the magnet's stability in proximity of plant equipment such as steel tanks and rotating equipment, and its sensitivity to elevated temperatures and UV radiation. The spectrometer was placed on the ground next to the SCT (see Figure 6.11a below) and left to adjust to the outside temperature, this took approximately 90 minutes. The shim, which indicates the magnetic field homogeneity, was not affected by the transfer between locations and remained stable throughout the day. This is exemplified in the spectrum shown in Figure 6.11b.

Figure 6.11 Trial of the *Spinsolve* outside laboratory conditions next to the SCT and in proximity to the OWETs. (a) Location of the *Spinsolve* while being trialled outside. (b) Spectrum obtained with the *Spinsolve* outside. Narrow linewidth and high sensitivity are evident.

Following initial performance checks, the normal day-to-day measurements with the SCT were resumed and NMR analysis carried out. The Spinsolve was operated outside for 10 hours demonstrating stable performance. Degradation is usually indicated by increased noise, signal loss, frequency shifts and decreasing magnetic field homogeneity leading to signal broadening, none of which was observed. Trialling the NMR spectrometer was thus a success showing the robustness of the system.

After set up and verification of the working condition of all analysis tools, routine sampling and analysis was performed from day four onwards. Typically, two sets of samples were taken from OWET B per day and measured with the three available methods of SCT-NMR, LLE-NMR and LLE-IR. The maximum number of SCT-NMR measurements achievable in the course of one shift was seven. The complete set of data points for oil-in-water concentration determined with the three methods during the field trial is presented in Figure 6.12.

Despite a few outlier measurements above 40 and below 18 mg/L oil-in-water, the overall consistency of the data points shown in Figure 6.12 is good. A trend of slightly increasing concentration within the first 2 thirds of the measurements can be identified (up to measurement 45) after which the oil-in-water concentration seems to drop. Apart from one high measurement on day 11, the IR spectrometer appears to read lower results than both NMR methods. This is most noticeable during the second half of the field trial.

For each day of measurements on-site, a daily average can be calculated summarising the results from the three methods SCT-NMR, LLE-NMR and LLE-IR. Figure 6.13 displays these daily averages of oil-in-water concentration and associated standard deviations. The fluid level in OWET B is also shown.

The results from the SCT-NMR and LLE-NMR methodologies are in good agreement. The IR measurements demonstrate increasing deviation towards the second half of the field trial as well as consistently lower values (one outlier) than the other two methods.

6.4 Field Trial with the Semi-Automated Prototype

Figure 6.12 Concentration of oil-in-water as determined with SCT-NMR, LLE-NMR and LLE-IR during the field trial. A total of 68 measurements were performed with SPE-NMR, 38 with LLE-NMR and 19 with LLE-IR. The secondary horizontal axis shows the days on site that correspond to the measurements.

Figure 6.13 indicates a correlation between the fluid level in the tank and the measured oil-in-water concentrations. As the tank level goes down, the measured oil concentration increases slightly. This is expected given that the hydrocarbons will tend to migrate towards the water surface over time and accumulate there. On day nine of the field trial, water from the Final Inspection Tank in the ETP was fed into OWET B to raise the level to 50 %. This water is essentially clean and it can be assumed that the liquids in the tank are diluted to some extent. The lower concentration measured during days 10 to 13 of the field trial is thus attributed to this dilution with cleaner water.

The routine sampling from OWET B and subsequent measurement using the SCT for solid-phase extraction and NMR spectrometer for analysis generated consistent results throughout the duration of the field trial. The results compared well against the alternative methods of LLE-NMR and, to a lesser extent, LLE-IR. The IR spectrometer Eracheck, however, had difficulties with the more complex nature of the oily water samples. During sample preparation, where mixing of the oily water samples with extraction solvent by means of vigorous shaking is required, emulsions of water-in-oil were formed that remained relatively stable. Figure 6.14a shows a photo of a typical emulsion formed during the LLE procedure.

For the NMR measurement, the presence of water in a sample is not a problem as long as the water peak does not overwhelm the relevant reference and target analyte peaks. As can be seen from Figure 6.14b, which presents a frequency domain spectrum of a LLE emulsified sample, some water is present but does not interfere with the analysis. For analysis with the Eracheck, water is a more severe problem as droplets that reach the measuring cell will scatter the infrared light source. This

Figure 6.13 Average concentration of oil-in-water as determined with SCT-NMR, LLE-NMR and LLE-IR through repeated measurements for the samples taken each day. On the second vertical axis, the liquid level in OWET B is plotted over the period of the field trial. Error bars represent plus/minus the standard deviation across repeated measurements where applicable.

can significantly impact or even inhibit measurements. During the field trial, emulsification of LLE samples presented a considerable problem for the Erachek effectively inhibiting measurements on some days.

Figure 6.14 LLE and yielded ^1H NMR frequency domain spectrum from the sample. (a) Sample of oily water and extraction solvent 1 % v/v CHCl_3 in PCE after shaking for LLE. Water droplets in the solvent phase are indicating that an emulsion has formed. (b) Frequency domain ^1H NMR spectrum showing the CHCl_3 reference peak along with some water contamination and the hydrocarbons extracted from the oily water sample.

With the intention to test the ability of the SCT-NMR methodology to capture varying oil-in-water concentrations, specifically in the lower range of what is expected for produced water, samples

Figure 6.15 Concentration of oil-in-water of 3 samples taken after and before the MBR and from OWET B, determined with SCT-NMR, LLE-NMR and LLE-IR. With respect to the SCT-NMR, average concentrations of oil-in-water resulting from twofold and triplicate measurement are given with error bars representing plus/minus the standard deviation across repeated measurements.

downstream of the OWETs were taken. One sample, "MBR Outlet", was taken in the ETP (refer to Figure 6.10) from a sampling point after the Membrane Bioreactor Package (MBR). A second sample, "MBR Inlet", was sampled after the treatment of Macro Porous Polymer Extraction (MPPE) and before the MBR. These 2 samples were extracted in the morning and analysed in 2 repetitions with SCT-NMR. A single measurement each with LLE-NMR and LLE-IR was also performed. Upon completion of these measurements, a third sample was taken from OWET B and analysed in triplicate with SCT-NMR, 2 measurements were conducted with LLE-NMR and one with LLE-IR. The results for the 3 samples determined with SCT-NMR, LLE-NMR and LLE-IR are shown in Figure 6.15.

Good consistency between the SCT-NMR measurements is exemplified by a low standard deviation for the low concentration samples. The standard deviation is slightly higher for the sample from OWET B. General agreement between SCT-NMR and LLE-NMR is good, the IR results are comparatively low for the samples taken downstream of the OWETs but agree well for the routine sample from OWET B. It is expected that the composition of the hydrocarbon contamination changes as the oily water is directed through the ETP due to removal of some hydrocarbons. As a result, some error will be introduced to the IR measurement as the calibration used to correlate the IR absorbance with hydrocarbon concentration was established with neat condensate in cyclohexane. With respect to the NMR measurement, only an increase in the aromatic content in the aqueous phase would present an issue with the chosen solvent mixture as the aromatic ring resonates at a similar frequency as the

Figure 6.16 Total oil concentration of samples from the CPI Inlet, MPPE Inlet, MBR Inlet and MBR Outlet measured with a Horiba instrument in the BMF lab over 2 months that overlap with the period of the field trial.

reference compound CHCl_3 . However, this is readily monitored with the NMR spectra and no peak broadening or appearance of a shoulder peak to the CHCl_3 resonance was observed.

Data was made available from the Woodside Pluto Burrup Materials Facility (BMF) laboratory for validation of the results obtained with the three methods used during the field trial. The BMF laboratory is responsible for routine sampling and analysis of the waste water in the ETP on Pluto LNG. Note that the measurements provided by the BMF lab were completed at different times and from other sampling locations to those used during the field trial. Figure 6.16 shows data of oil-in-water concentration of samples taken from the CPI Inlet, the MPPE Inlet as well as the MBR Inlet and Outlet determined with a Horiba instrument (infrared spectrometer) at the BMF lab.

Figure 6.16 demonstrates a clear trend of decreasing oil concentration as the water passes through the treatment stages of the Effluent Treatment Plant. The CPI unit (first primary treatment after the water exits the OWETs) removes dispersed oil; droplets below $\approx 40 \mu\text{m}$ and any dissolved oil remain in the water. The MPPE package provides an extraction process where the extraction liquid is immobilised in a macros-porous polymer medium. As the contaminated water passes through, some retention of low polarity components occurs. Downstream of the MPPE, the contaminated water is treated in the MBR package with micro-organisms that break down the organic pollutants. After the MPPE, the oil concentration in the water as determined with the Horiba instrument is around 20 ppm and subsequently reduced to below 10 ppm in the MBR. The intermediate stages — CPI and MPPE — do not remove hydrocarbon contamination to below a defined value. The achievable reduction in oil

Figure 6.17 Total oil concentration of samples from the CPI Inlet as determined by BMF lab (Woodside, IR) analyses showing historical and current data compared to OWET B daily averages measured with SCT-NMR.

concentration depends on the initial oil concentration in the CPI feed as well as other parameters, such as additional chemicals present, temperature, presence and size of oil droplets.

During the field trial, the majority of the samples analysed with SCT-NMR, LLE-NMR and LLE-IR were taken directly from OWET B. As the other oily water tank — OWET A — was off-line before, throughout and after the field trial, the conditions of the sampling point located at the CPI Inlet roughly match those at OWET B. Oil concentration for the CPI Inlet as determined by the BMF lab with a Horiba infrared spectrometer are compared against the results from SCT-NMR for OWET B in Figure 6.17.

The measurements of SCT-NMR show reasonably good agreement with the results from the BMF lab. The SCT-NMR method records a reading approximately 4 mg/L lower than the Horiba device, however, the differences in sampling location and sample preparation must be considered.

Figure 6.18 compares the results from the Horiba device against the SCT-NMR method for samples taken downstream of the OWETs in the ETP before and after the MBR.

Agreement in Figure 6.18 is excellent at the MBR Inlet. Here, the SCT-NMR measurements are in line with the trend exhibited by the Horiba measurements. The measurements of the samples taken after the MBR package (MBR Outlet) show a large deviation between the Horiba and SCT-NMR results. The Horiba reads oil concentrations that are consistently around 5 mg/L whereas the SCT-NMR methodology determines 15 mg/L oil-in-water. This deviation between the NMR method and the Horiba measurements is significant. As previously detailed (see Section 3.8), SPE in

Figure 6.18 Oil-in-water concentration for the MBR Inlet and Outlet determined in the BMF lab with the Horiba instrument versus measurements conducted with SCT-NMR. The SCT-NMR results are shown as sample averages.

combination with NMR analysis was routinely used to determine oil concentrations at 5 mg/L and lower, showing that the methodology is able to capture oil-in-water content down to 1 mg/L. Contributions to the large divergence can originate from the sampling procedure, specifically the inevitable time delay between sampling and measurements with the Horiba instrument. As with the measurements conducted with the Eracheck, additional uncertainty is inevitably introduced to the Horiba measurements due to different compositions of the hydrocarbons in the calibration samples and in the actual water samples.

Overall, testing of the semi-automated prototype implementing the SPE-NMR approach for oil-in-water analysis was a success. All of the equipment was straightforward to install and start up and performed without failure or major problems despite being exposed to demanding environmental conditions. The SCT was not affected by the chemicals or solids that were present in the oily water samples taken from OWET B. The SCT-NMR measurements compared favourably against the alternative methods of LLE-NMR and LLE-IR. Specifically, the methodology was shown to be immune to sample contents that can complicate alternative methods, for example the tendency of the oily water samples to form stable emulsions significantly affected the IR measurement. In addition to the routine measurements in the range of 25 - 30 mg/L oil-in-water, it was demonstrated that the SCT-NMR methodology captures varying concentrations and in particular concentrations below 20 mg/L. Reference data was provided by the BMF lab to extend the validation of the SCT-NMR results against alternative methods. Oil concentration of samples taken at the CPI Inlet and the MBR Inlet

determined with the Horiba instrument compared well with the SCT-NMR methodology and provided verification of the results obtained.

After laboratory testing and a successful field trial using the semi-automated SCT-NMR prototype for oil-in-water analysis, incorporating the NMR spectrometer into the SCT to provide a fully automated measurement was the next logical step. The measurements with the fully automated prototype are described in Section 6.5 below.

6.5 Fully Automated OiW Analysis with SPE-NMR

The measurements thus far discussed in this chapter were generated using initially the manual approach (Sections 6.1 and 6.2) and after development of the semi-automated prototype, deploying the thereby automated SPE procedure in combination with a manual NMR measurement (Sections 6.3 and 6.4). Upon demonstration that the semi-automated prototype was able to extract and pre-concentrate the hydrocarbon contamination of both artificial samples and field samples, the NMR measurement was incorporated as part of the prototype to provide a fully automated SPE and NMR measurement procedure. This is hereafter referred to as "auto-SCT-NMR". The setup of the flow-through NMR measurement and the individual steps required to conduct the auto-SCT-NMR analysis were described previously in Section 5.3. In the following, details of the experiments performed on different contaminated water samples via auto-SCT-NMR and validation of the same samples with alternative methods are given. Subsequently, the results are presented and discussed.

6.5.1 Experimental Setup

With the intention to investigate the ability of the auto-SCT-NMR approach to determine the hydrocarbon content in water, a variety of artificial produced water samples were analysed. A Western Australian light crude oil and a (locally sourced) condensate were available as contaminants. A total of 9 independent samples of either crude oil — A - E — or condensate — F - I — dissolved in deionised water were prepared. Approximately 2 L of deionised water was transferred to a 2 L Schott bottle, an excess amount of one of the two contaminants was added (2 - 5 ml) and the two phases mixed with a homogeniser at 10,500 rpm for one minute. The sample bottle was then capped and left to equilibrate overnight. During this process, the excess oil formed an insoluble layer on the water surface, which was not removed for the measurements in order to provide a barrier to potential contaminant evaporation.

For one set of measurements, one sample was analysed in several repeats with the auto-SCT-NMR procedure over a period of 5 - 7 hours. The measurement protocol as applied during these experiments can be found in Section 5.3.4.

Concurrent to the auto-SCT-NMR, analysis was performed with IR, using the benchtop Eracheck device equipped with a quantum cascade laser, and GC-FID. The GC-FID was the previously used Thermo Scientific™ Trace™ 1300 GC equipped with a flame ionization detector and autosampler. The capillary column was a TraceGold TG-5MS column (30 m x 0.25 mm i.d.) with a nominal film thickness of 0.25 μm . Both the IR spectrometer and the GC-FID apparatus were calibrated beforehand with four calibration samples each of neat condensate and crude oil in the extraction solvent cyclohexane. Calibration curves were established correlating (i) measured IR absorbance with oil-in-solvent concentration and (ii) integrated peak area between retention times of 7.9 and 22 min with oil-in-solvent concentration for the IR spectrometer and GC-FID, respectively. Extraction of the hydrocarbon contamination from the sample was initially performed with liquid-liquid extraction. In order to ensure better comparability of the sample composition, the LLE procedure was subsequently replaced by solid-phase extraction with Prevail C18 cartridges (distributed by PhaseSep Pty Ltd, Australia). A four channel peristaltic pump (Ismatec REGLO-ICC) was deployed for loading and elution of the cartridges at a flow rate of 5 ml/min. Each measurement was conducted using a fresh cartridge, applying a loading volume of either 150 or 200 ml and then eluting with 15 ml of cyclohexane. The extract obtained was then promptly analysed in two repetitions with the IR spectrometer. A small portion of the extract was transferred to two sample vials (approximately 1.5 ml each) for GC-FID analysis. Here, the time delay between sample preparation and measurement varied between one to 12 hours due to restricted equipment access. Typically, two SPE-IR/GC measurements were conducted on each contaminated water sample; one in parallel with the first and the second concurrent to the fourth or fifth auto-SCT-NMR measurement. The inlet tubing for the sample pump of the SCT and the one for the peristaltic pump deployed for the manual SPE procedure were inserted into the sample to the same height. Thereby, it was attempted to perform both measurements with consistent sample compositions.

6.5.2 Results and Discussion

Initially, a preliminary set of measurements were conducted during which the sample preparation for the IR and GC-FID analyses was accomplished with liquid-liquid extraction. During this procedure, a volume of roughly 300 ml was separated from the bulk sample prior to connecting the sample bottle to the SCT and initiating the auto-SCT-NMR measurements. This portion was transferred to a separating funnel and the liquid was allowed to settle for five minutes. From the bottom of the separating funnel, 150 ml were decanted into a 250 ml Schott bottle and 15 ml of the extraction solvent cyclohexane was added. The bottle was capped and shaken vigorously for five minutes. After phase separation had occurred, the solvent extract was measured twice each with the IR spectrometer Eracheck and the GC-FID. A second LLE and subsequent analysis was conducted with the residual sample upon completion of the auto-SCT-NMR analysis. Figure 6.19 summarises the individual

measurements of oil-in-water as determined through auto-SCT-NMR, LLE-IR and LLE-GC-FID (referred to as LLE-GC) analysis.

Figure 6.19 Oil concentration in a sample of crude oil dissolved in deionised water as determined with auto-SCT-NMR, LLE-IR and LLE-GC.

The four auto-SCT-NMR measurements average to a value of 8.9 ± 2.4 mg/L oil-in-water and thus show good agreement across repeated measurements. However, the two alternative methods yield values with significant discrepancy to the auto-SCT-NMR results. This is more pronounced for the fourth data point where the variation is > 30 mg/L, mutually confirmed by IR and GC-FID. The discrepancy observed for this initial trial run was repeatable throughout the next measurement sets. As a consequence, the sampling and sample preparation protocol was investigated more closely, which led to the conclusion, that the sample composition analysed during the auto-SCT-NMR measurements is not comparable to that measured with LLE-IR and -GC. After equilibration time overnight, the bulk contaminated water sample develops an insoluble oil layer on top of the water surface as well as a concentration gradient due to migration of the contained oil towards the surface. When a portion of the sample is separated from the bulk for LLE and transferred to a separating funnel, agitation is re-induced disturbing the equilibrium between the oil and water phase. The time interval of 5 min allowed for settling in the separation funnel is not sufficient to re-establish the equilibrium and due to the different liquid to volume ratio, will further cause a diverging sample composition to the bulk sample. Similarly, analysis of the residual sample upon cessation of the auto-SCT-NMR measurements is expected to yield a significantly different and notably higher oil content. The sample pump of the SCT-NMR device pumps the sample out from the bottom of the bottle, thereby slowly lowering the liquid level of the bulk. However, the portion of the sample used to successively load the SPE cartridges was always representative of the currently lowest oil concentration in the sample due

to the oil migrating upwards. After the last auto-SCT-NMR measurement, the residual sample including the insoluble oil layer was transferred to a separating funnel. Again, agitation was induced and, more importantly, the fraction of the sample, that naturally contains the highest oil content because of its closeness to the water surface, was analysed. These effects leading to a significant discrepancy between the auto-SCT-NMR and LLE-IR/GC measurements have been reported previously when using the semi-automated prototype for analysis (refer to Section 5.2.4 where the laboratory testing of the SCT-NMR method is discussed). Therefore, the sample preparation was modified; LLE was replaced by SPE using the established procedure (refer to Chapter 3) with the commercial, reversed-phase SPE cartridges. The inlet tubing for the peristaltic pump was inserted into the bulk sample to the same depth as the tubing for the SCT device and loading for the manual SPE procedure performed concurrently to the loading for the auto-SCT-NMR procedure. It is thus expected to achieve a comparable sample composition for the IR and GC-FID analyses. The preliminary trial run showed good agreement across the three methods of SPE-IR, SPE-GC-FID (referred to as SPE-GC) and auto-SCT-NMR. Consequently, it was progressed to conduct extensive testing of 10 samples of crude oil and condensate, respectively, in deionised water.

The first set of experiments was conducted using the five samples A to E of crude oil dissolved in deionised water. In order to investigate the solvent reusability and its effect on the accuracy of the results, solvent recycling during the auto-SCT-NMR measurements was implemented for the last two samples D and E. As outlined in Section 5.3.4, before elution of the SPE cartridge, a baseline measurement of the solvent supply was performed to assess the contained oil. Then, the elution step was initiated and measured in the NMR in the same way as without solvent recycling. During data analysis, the oil peak of the baseline measurement was subtracted from the elution measurement and thereby, the oil extracted from the water sample can be inferred. Figure 6.20 below shows the individual measurements of two samples B and E as determined with auto-SCT-NMR without and with solvent recycling, respectively. Validation data points as measured with SPE-IR and SPE-GC are also presented.

Consistency across the repeated auto-SCT-NMR measurements is generally good with a slightly varying oil-in-water concentration observed for both samples. The liquid level of the sample bottle drops as a function of load volume applied as successive SPE procedures are performed. Due to the concentration gradient across the sample with a higher concentration at the top below the water surface and the decreasing liquid level, the oil content at the point where the sample was pumped out was expected to slowly increase. However, at the same time, some loss of hydrocarbons via evaporation inevitably took place. Therefore, the composition of the sample volume that was applied during the loading step of the SPE procedure will change between the measurements as a continuous attempt to (re)establish an equilibrium existed.

Figure 6.20 Oil concentration of samples (a) B and (b) E as determined with auto-SCT-NMR, SPE-IR and SPE-GC. Solvent recycling has been deployed during auto-SCT-NMR for analysis of sample E.

Agreement between the auto-SCT-NMR and the two alternative methods is excellent for sample B (Figure 6.20a) and good for sample E (Figure 6.20b), the slightly varying oil content is mutually reflected by the three methods.

With the intention to investigate the impact of the sample preparation on the oil-in-water results, sample C was analysed deploying an expanded range of measurements. At first, the typical auto-SCT-NMR along with the SPE-IR and -GC measurements were carried out; the results are presented in Figure 6.21 below.

A difference for the first measurement with auto-SCT-NMR and SPE-IR/-GC of approximately 8.5 mg/L can be observed, whereas the readings for the last measurement (#6) show excellent agreement. For the first SPE in the auto-SCT-NMR procedure, a new cartridge was installed that had not been used before. During the loading and elution step, an unusually large pressure drop across the cartridge was recorded. As a consequence, it must be assumed that the thus obtained oil-in-water concentration has a higher uncertainty and does not reflect the actual concentration in the sample.

A deviation from the slightly decreasing trend of measurements #1 to #5 is observed with the last measurement #6. This, however, can be assumed to reflect the variability of results that are obtained when measuring oil-in-water over time.

Following measurement set #6 in Figure 6.21 were additional analyses of the residual sample using LLE in combination with NMR, IR and GC-FID. The solvent extract obtained during the last auto-SCT-NMR procedure (#6) was retained and analysed via a manual NMR measurement essentially replicating the procedure previously applied for SCT-NMR measurements. This was done to assess the ability of the flow-through NMR setup to accurately determine the oil content of a sample. Table 6.4 compares the oil content as determined via seven separate measurements of auto-SCT-NMR, SCT-NMR, SPE-IR, SPE-GC as well as LLE in combination with NMR, IR and GC-FID.

Figure 6.21 Oil concentration of sample C as determined with auto-SCT-NMR, SPE-IR and SPE-GC.

Table 6.4 Comparison of the OiW concentration of sample D determined with NMR, GC-FID and IR using SPE on the bulk sample or LLE performed with the residual sample after SPE analyses. SCT-NMR refers to automated solid-phase extraction using the SCT followed by manual NMR measurement of the solvent extract.

	SPE				LLE		
	auto-SCT-NMR	SCT-NMR	IR	GC-FID	NMR	IR	GC-FID
OiW [mg/L]	7.3	10.7	8.2	7.1	41.8	57.3	55.0

The values in Table 6.4 exhibit good agreement across the four measurements deploying SPE for sample preparation with a standard deviation of ± 1.4 mg/L. In accordance with previous results, liquid-liquid extraction yielded a significantly higher oil content which is mutually reflected for the three analysis methods deployed. Again, this can be explained with the experimental procedure deployed. The residual sample inclusive of the insoluble oil layer on the water surface was transferred from the sample bottle to a separation funnel. After a settling time of approximately ten minutes, 150 ml were decanted for LLE-NMR followed by 150 ml for LLE-IR and -GC. The latter sample was taken from beneath the water surface, hence due to the proximity to the insoluble oil layer a higher oil content compared to prior samples is anticipated. This is confirmed with the lower reading of the LLE-NMR measurement. In order to eliminate the possibility that the SPE procedure does not retain all hydrocarbons from the aqueous phase and therefore gives lower results than LLE, water was sampled from the exit of the SPE cartridge during the loading stage of auto-SCT-NMR measurements. This water was then subjected to LLE with cyclohexane and the solvent extract analysed with the IR

spectrometer. No IR absorbance was recorded confirming that all relevant hydrocarbon content in the samples is retained during solid-phase extraction with the Prevail C18 sorbent.

Figure 6.22 summarises the experiments with the five samples of crude oil dissolved in water presenting the average oil content for the independent samples as determined with auto-SCT-NMR, SPE-IR and SPE-GC. Where applicable, error bars that represent the standard deviation across repeated measurements on the same sample are shown.

Figure 6.22 Average oil concentration in samples A to E as determined with auto-SCT-NMR, SPE-IR and SPE-GC. Error bars show the standard deviation across repeated measurements where applicable.

Agreement across the three analysis methods is reasonably good, a considerably discrepancy between the auto-SCT-NMR results and those obtained via SPE-IR and -GC analysis is only observed for sample D. Here, the standard deviation for the repeated auto-SCT-NMR measurements is relatively large at $> 30\%$ of the average $c_{oil,NMR,D} = 25.4$ mg/L compared to the other sets. Note that samples A – C and E were consistently measured at 22 mg/L and lower, whereas sample D showed an initially higher oil content which increased throughout the course of the measurements. It is assumed that this initially high oil concentration resulted in a greater variation of the sample composition as the measurements progressed.

To further explore the ability of the auto-SCT-NMR approach to determine oil-in-water content, experiments were conducted with four independent samples of a locally sourced condensate dissolved in water. Again, it was attempted to conduct measurements both without (samples F and I) and with (samples G and H) solvent recycling in the SCT-NMR device and validate the results via SPE-IR and SPE-GC analysis. Typical results of the individual measurements performed are shown for samples G and I in Figure 6.23.

Figure 6.23 Oil concentration of samples (a) G and (b) I as determined with auto-SCT-NMR, SPE-IR and SPE-GC. Solvent recycling was deployed during auto-SCT-NMR for analysis of sample G.

Consistency across the repeated auto-SCT-NMR measurements is good for both samples, a slightly greater variation of the measurements can be observed for sample G. SPE-IR and SPE-GC analyses show some discrepancy from the auto-SCT-NMR results for the individual measurements, specifically with respect to sample I. However, this reflects the general difficulty of directly comparing different measuring principles for the determination of oil content in produced water. Delay times between sample preparation and measurement during which the sample might be exposed to air and thereby inducing contaminant loss due to evaporation as well as the measuring principle applied need to be taken into account. Looking at the average determined for a sample through repeated measurement (see below, Figure 6.24) gives a better indication with respect to agreement of results. Therefore, the individual measurements are condensed to provide the average oil content of samples F to I as determined with auto-SCT-NMR, SPE-IR and -GC and are presented in Figure 6.24.

Figure 6.24 shows reasonably good agreement across the three methods. However, it can be discerned that auto-SCT-NMR measurements with solvent recycling (samples G and H) yield consistently lower results than SPE-IR and SPE-GC analyses. Referring back to Figure 6.22, samples D and E exhibited the same trend. The application of reused solvent during the auto-SCT-NMR procedure involves the measurement of a baseline spectrum to assess the contamination in the solvent before proceeding to the elution step. Subsequently, this baseline spectrum is subtracted from the spectrum of the solvent extract to obtain the actual amount of oil extracted from the sample. For this to yield accurate results, equally good quality of the baseline and the solvent extract spectrum is required. Note that shimming is not repeated between the baseline measurement and the elution. Throughout the course of the experiments, fluctuations in the quality of the NMR spectra have been observed that were reflected as decreased SNR and peak broadening. This can be caused by a sudden change in the surroundings, for example if equipment in proximity to the NMR spectrometer is switched on or off, which would essentially require adjustment of the shim. Additional shielding of the magnet can also reduce the impact of changes in the surrounding conditions. Ultimately, when

Figure 6.24 Average oil concentration in samples F to I as determined with auto-SCT-NMR, SPE-IR and SPE-GC. Error bars show the standard deviation across repeated measurements, if applicable.

applied in the field, it is expected that the magnetic field homogeneity remains more stable, specifically for subsea deployment where noise is minimized and temperature fluctuations are negligible.

Besides assessing the ability of the auto-SCT-NMR procedure to accurately determine the oil content in contaminated water samples, preliminary recycling of the SPE cartridges used in the fully automated prototype was investigated. To this effect, cartridges were reused several times both for the analysis of the same sample in successive measurements and for different samples. The time delay between measurements varied randomly with up to several days during which the cartridges were not in use. No conditioning or other treatment was performed on the cartridges. For validation purposes, each sample was measured at least once using a new cartridge. Thus far, a maximum of 20 uses with one SPE cartridge was achieved without showing signs of degradation. The pressure drop across the cartridge remained constant throughout and the oil-in-water results obtained were consistent with the validation measurements. There is every indication that the SPE cartridges as deployed in the fully automated prototype for SPE-NMR measurements can be reused beyond 20 times. This, however, has to be confirmed through extensive testing in future measurements.

6.6 Conclusion

The robustness of the SPE-NMR approach to determine the oil content in produced water was investigated via extensive laboratory testing and a field trial at an onshore gas plant. Initially, the

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feasibility of reusing the SPE cartridges and the NMR solvent was assessed using the manual SPE-NMR procedure. Upon completion of the semi-automated prototype (SCT-NMR), laboratory tests were conducted with artificial samples of oil in water as well as field samples from a local gas production facility. Furthermore, the semi-automated version of the prototype was trialled in the field to show its ability to withstand field conditions while still delivering accurate oil-in-water measurements. The thus far manual NMR measurement was then incorporated as an in-line measurement in the prototype to provide fully automated SPE-NMR measurements (auto-SCT-NMR). Successful testing on a range of independent contaminated water samples was performed and validated against the two alternative methods of IR absorbance and gas chromatography with flame ionisation detection.

The preliminary recycling measurements with the solvent and the SPE cartridges demonstrated the potential to be repeatedly used over an extended time period. This is considered essential for the application of an automated SPE-NMR device in the field in order to minimise maintenance and maximise lifetime. In this context, additional measurements were conducted with the semi-automated and later with the fully automated prototype. The implementation of (refillable) SPE cartridges with stainless steel housing in the prototype did not limit the ability to reuse the cartridges for multiple SPE procedures without loss of retention capacity. However, further experiments are required to increase the number of reuses and to investigate the impact of other constituents in the produced water, specifically the presence of solids.

Throughout the field trial, the equipment involved in the SCT and the NMR spectrometer performed without failure or major problems despite being exposed to demanding environmental conditions. The SCT-NMR measurements compared favourably against the alternative methods of LLE-NMR and LLE-IR as well as the data provided from an off-site laboratory. Similarly, consistent measurements were achieved in the laboratory using the advanced prototype that provides fully automated SPE-NMR analysis. The oil content of a variety of samples, contaminated with either an aliphatic crude oil or a condensate, was determined using auto-SCT-NMR measurements and successfully validated against the alternative methods of SPE-IR and SPE-GC.

Despite the capability of the fully automated SCT-NMR prototype to provide reliable and accurate oil-in-water measurement, the extensive laboratory and field testing indicated where optimisation is required to exploit the full potential of the system. For example, the electrically actuated, three-way ball valves show a deficit due to their configuration and large orifice compared to the predominantly used tubing size of 1/8 inch. This results in carry-over when switching between the positions and thereby mixing of the solvent and aqueous phases. Furthermore, due to several transitions between tubing sizes, regions with high potential of fluid accumulation exist that cannot be removed via compressed air flushing. Optimisation of system components is recommended to enhance the ability to perform measurements using a consistent and repeatable procedure.

Chapter 7

Conclusion and Outlook

This chapter provides a summary of the work performed as part of this doctoral research. Concluding remarks are presented in Section 7.1 followed by recommendations regarding future work in Section 7.2.

7.1 Conclusion

The main objective of this doctoral research was the development and testing of a novel approach to quantitatively determinate the oil content in produced water using solid-phase extraction in combination with benchtop NMR analysis. Literature research revealed the lack of robust and reliable oil-in-water monitoring devices in the oil and gas industry, specifically with regards to application in remote locations with limited operator intervention. Given recent advancements in magnet design of low-field NMR spectrometers that led to enhanced resolution and sensitivity, additional options for the application of NMR as an analytical tool outside of the laboratory opened up. As opposed to most measuring principles deployed for oil-in-water monitoring, ^1H NMR provides a non-optical measurement that can detect dissolved and dispersed oil components as well as both the aromatic and aliphatic constituents. In combination with solid-phase extraction to extract the oil from the produced water and pre-concentrate it into a suitable solvent, this approach, referred to as SPE-NMR, is considered promising for oil-in-water compliance monitoring in the oil and gas industry. Based on the proof of concept in the laboratory, a working prototype to implement the methodology and provide fully automated measurements was constructed, tested and validated.

The focus of Chapter 3 of this thesis is the proof of concept of the proposed SPE-NMR methodology for oil-in-water metering. A suitable operational procedure was developed for the solid-phase extraction in the laboratory involving a simple peristaltic pump and the application of commercially available SPE cartridges. Optimisation of the SPE procedure was carried out in order to minimise the timescale of sample preparation while ensuring maximum extraction (hydrocarbons

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from the aqueous phase) and recovery (removal of hydrocarbons from the SPE sorbent) efficiency. A solvent mixture consisting of 1 % CHCl_3 in tetrachloroethylene was selected to elute the SPE cartridges and subsequently conduct the NMR analysis with the obtained solvent extract. This mixture enables accurate quantification of light crude oils in an effectively self-calibrated measurement. It was shown that the SPE-NMR method compared favourably against the alternative methods of IR absorbance and gas chromatography. Repeatable and accurate oil-in-water measurements were achieved over the range stipulated by current produced water discharge regulations. Furthermore, the simple laboratory setup deployed for these proof of concept tests demonstrated the potential to convert the manual SPE-NMR method into a fully automated procedure.

Following the proof-of-concept of SPE-NMR for the determination of total oil in produced water, the methodology was extended to allow the separate quantification of aromatic and aliphatic hydrocarbon contributions to the total oil content (Chapter 4). This is referred to as Advanced SPE-NMR. The oil-in-water monitoring devices developed for field application in the oil and gas industry generally measure either the aromatic or the aliphatic hydrocarbons and then infer the total oil content thereof. Furthermore, calibration is generally required to correlate the property that is measured with the oil content in the sample. The Advanced SPE-NMR method, developed in the context of the work presented here, involves a twofold measurement with two solvent mixtures, both containing the reference compounds HMDSO and CHCl_3 but at different ratios. Thereby, the self-calibrated character of the original approach is retained while allowing the separation of the total oil into the aromatic and aliphatic fractions. Successful application of the Advanced SPE-NMR methodology to the analysis of simulated produced water samples containing a mainly aliphatic crude oil along with a spike of toluene was demonstrated. Again, validation against well-established alternative techniques, namely GC-FID and IR, was carried out and showed generally good agreement.

Chapter 5 describes the design and construction process of a working prototype to convert the manual SPE-NMR approach into a fully automated procedure. Initially, a semi-automated version was built that performs automated solid-phase extraction but requires a manual NMR measurement. The SPE device was constructed as a robust and mobile apparatus, which is referred to as the SCT (self-contained transportable). The SCT was built in-house using mostly commercially available components to partially facilitate future replication of the system. With the intention to confirm functionality and robustness of the semi-automated prototype, the SCT was tested extensively both in the laboratory and in the field before proceeding to full automation. Thus, after confirmation that the SCT can reliably and accurately determine the oil-in-water content of produced water samples, it was extended to include the NMR spectrometer to provide an in-line measurement. This auto-SCT-NMR prototype is automated via computer using a LabVIEW program that enables the user to control the steps of the SPE procedure, NMR measurement and subsequently retrieve oil-in-water results generated by a post-processing and analysis algorithm.

The final chapter (Chapter 6) presents extensive laboratory testing with the semi-automated (SCT-NMR) and the fully automated (auto-SCT-NMR) prototype as well as onshore field trialling of the semi-automated prototype. The components incorporated in the prototype as well as the measurements themselves proved to be robust when exposed to field conditions and under application to a variety of (field) samples. In the field, measurements using LLE in combination with IR along with data obtained from an independent off-site laboratory provided confirmation of the SCT-NMR results. In the laboratory, the SCT-NMR measurements were validated against both LLE and SPE in combination with IR and GC-FID analyses and compared favourably. A variety of samples was used to test the performance of the SCT-NMR prototype, this included simulated produced water samples as well as locally sourced field samples. Similarly, the fully automated prototype was subject to extensive laboratory testing with samples of crude oil and condensate in water and a measurement protocol for operation of the system was established. SPE-IR and SPE-GC-FID measurements were conducted in parallel with auto-SCT-NMR analysis on the same samples and provided confirmation of the results. Furthermore, preliminary tests were conducted to investigate the capability of the SPE sorbent material to be reused multiple times for the extraction of hydrocarbons from aqueous samples. This was done with regard to potential future commercialisation of the system as an autonomous monitoring device where the lifetime of the device without human intervention needs to be maximised. Recycles of up to 30 and 20 were achieved with the commercial and the SPE cartridges integrated in the prototype, respectively. No signs of degradation were observed and thus reusage of up to 100 times can be considered feasible. Similarly, cycling of the NMR solvent was investigated. With the initial manual SPE-NMR approach, the maximum oil concentration in the solvent that still enables the accurate assessment of oil-in-water content was determined. Scale-up calculations with the results of recycling both SPE sorbent and NMR solvent demonstrated that autonomous operation of up to 4.5 years can be achieved with a suitable SPE-NMR device. Lastly, preliminary solvent and SPE cartridge reusability was implemented with the fully automated prototype demonstrating that this is feasible in the current setup.

7.2 Future Work

In the context of this research, a novel approach consisting of solid-phase extraction in combination with benchtop NMR analysis to measure the oil content in produced water was developed, optimised and converted into a fully automated, working prototype. The suggestions for future work are based on the experimental work conducted with the SPE-NMR prototype both in the laboratory and in the field.

Future work regarding the fully automated prototype should focus on extending the range of measurements to include a wider variety of samples, in particular field samples. Thus far, predominantly simulated produced water samples consisting of either a light crude oil or condensate

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dissolved in deionised water were used. Field samples with a more complex composition due to the presence of additional, non-oil components such as salts, MEG or solids, should be analysed with the auto-SCT-NMR method. The intention here should be the demonstration of the capability to provide self-calibrated oil-in-water measurements for different hydrocarbon sources and varying sample composition. Validation against alternative, well-established analysis methods is, of course, advised. As part of additional measurements over a wider range of samples and conditions, it is also suggested to explore how the errors in reproducibility, that are inherent to oil-in-water measurements and were shown to significantly affect the measurements performed for this doctoral research, can be reduced. For example, the addition of surfactants to the artificially prepared contaminated water samples would allow to dissolve a known amount of an oil contaminant and therefore facilitate comparison of results obtained with SPE-NMR against known concentrations. Uncertainty calculations, such as the one performed for the Advanced SPE-NMR methodology, could be used to evaluate the uncertainty of the SPE-NMR method as well as alternative, well-established methods such as IR and GC-FID in order to point to potential improvements in the experimental procedure

Extending the measurements with the fully automated prototype should also be used to optimise the operational procedure. This might lead to the replacement of some system components and/or the addition of components to complement the setup and provide additional functionality. The testing of the (semi-)automated prototype revealed deficiencies associated with some of the built-in components and the implemented flow path. Specifically, the three-way, electrically actuated ball valves and the frequent transition between different tubing sizes introduce regions where fluid can accumulate undisturbed by the compressed air flush. This causes mixing of the solvent and the aqueous phase, which reduces the consistency and hence accuracy of the successive NMR measurement. Substituting the ball valves with similar valves that have a smaller orifice and do not induce carry-over when switching between positions should be considered. Minimising the mixing of the two phases to a negligible extent would render the measurement protocol more repeatable, thereby enhancing the accuracy of the oil-in-water measurements conducted with the auto-SCT-NMR. Alternatively, the setup of the prototype could be amended by addition of a mixing and gravity separation cell. A potential flow diagram to achieve this is shown in Figure 7.1.

P = piston pump, MFC = mass flow controller, V = actuated 3-way ball valve, MV = manual 2-way ball valve, GS = gravity separator (cylindrical)

Figure 7.1 PFD of the SPE and NMR analysis procedure setup to provide an automated prototype. The original design is complemented with a gravity separation cell for improved measurements. MFC = mass flow controller, V1 - V6 = electrically actuated ball valves, P1 and P2 = piston pumps for solvent and sample, respectively, MV1 and MV2 = manual 2-way ball valves, GS = gravity separator (cylindrical).

As indicated in the PFD, the small volume (maximum 50 ml) cell should be placed in between the SPE cartridge and the NMR spectrometer, preferably elevated compared to the latter. The bottom of the cell could be equipped with a simple two-way valve and the outlet tube directed into the NMR spectrometer. During the elution stage of the SPE procedure, the solvent extract would be collected in the cell before progressing to the NMR measurement. As a consequence, the heavier solvent phase would accumulate at the bottom while any residual water can migrate to the top. Once phase separation is complete, the solvent phase can be directed into the NMR spectrometer under gravity. This would not only allow better separation of the solvent and aqueous phase but also enhance mixing of the solvent extract to provide a more homogeneous sample for measurement. Additional components can be readily incorporated into the existing computer program for automation purposes.

Investigations into system robustness to solids need to be an integral part of the optimisation process. Future work could focus on monitoring solids transport through the system with a particular interest in the trajectories developing inside the SPE cartridges. Velocity mapping with NMR and Magnetic Resonance or X-ray Imaging could be applied to visualise and better understand potential flow channelling and deposition of particles in the sorbent matrix.

It would also be of interest to examine other sorbent materials in order to expand the range of compounds in produced water that can be detected and potentially quantified. Over recent years, environmental discharge regulations have been trending towards stricter limits and tighter restrictions on the more harmful constituents, this is exemplified by the Norwegian "Zero harmful discharge

regime". Current legislative requirements for reporting of quality of discharged produced water focus on the non-polar hydrocarbon content in produced water (e.g. refer to the technical guidance regarding the analysis methodology in the UK [39]). However, polar hydrocarbons, predominantly in the form of organic acids, can also be present in produced water at significant concentrations [224]. Some of the organic acids consist of a mixture of low molecular weight carboxylic acids that are readily biodegraded and therefore are not of environmental concern [214]. However, naphthenic acids — carboxylic acids with saturated or aromatic ring structure — can also be present in produced water as part of the dissolved and/or dispersed hydrocarbons. Naphthenic acids act as surfactants [225], hence can contribute to the stability of dispersed oil in water, and have been shown to have toxic effects on a variety of organisms [217, 226, 227]. It has been reported that they contribute to the aquatic toxicity of produced water [228] and are not readily removed by conventional produced water treatment technologies [229]. Therefore, the measurement of organic acids, in particular naphthenic acids, can be considered of significant interest to the oil and gas industry. In order to quantify naphthenic acids in produced water, the SPE-NMR approach presented in this doctoral thesis can be applied. Modifications will be required regarding the sorbent used in the SPE procedure as well as the solvent deployed for elution and subsequent NMR measurement. Suggested SPE sorbents include octadecyl bonded silica C18 [230] — already deployed here for the analysis of total oil content in produced water — and Isolute®ENV+ (Biotage AB, Sweden), a hyper crosslinked hydroxylated polystyrene-divinylbenzene copolymer, specifically designed to target polar analytes in aqueous sample matrices. ENV+ has also been previously applied for the extraction of naphthenic acids from water samples [231, 228]. As it is known that C18 sorbents are able to retain a wide range of hydrocarbons, non-polar and weakly polar components, the ENV+ is considered more appropriate. However, the combination of two (or more sorbents) should be explored to selectively target the analyte of interest. For example, a C18 cartridge could be used in series with ENV+ in order to capture the non-polar hydrocarbons from the sample in the first cartridge and then retain the polar compounds, i.e. any acids, in the ENV+ cartridge. In regards to the solvent choice for elution of the acids from the sorbent and quantitative analysis with NMR, a reference compound with a suitable chemical shift is required. Naphthenic acids resonate at several frequencies in ^1H NMR due to their OH-, methyl and methylene as well as aromatic functional groups. Thus, a reference compound with a single, sharp resonance either $\delta < 0$ ppm or $\delta > 10$ ppm is desired. First investigations, however, need to focus on a better definition of the composition/structure of the targeted naphthenic acids and then suitable NMR reference compounds can be explored accordingly.

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Appendix A

Measurement Uncertainty

In order to specify all uncertainties contributing to the parameters of the measurement equation have to be considered [220, 232]. Estimation of the uncertainty associated with the SPE-NMR methodology is derived below. This is followed by calculations to determine the uncertainty related to the gravimetric preparation of the standard samples.

Advanced SPE-NMR Measurement

For the assessment of a mass m_X of a target species in quantitative NMR, the following equation is applied in the context of the work presented here (note Equation 2.22 is repeated here for reasons of clarity):

$$m_X = m_{ref} \frac{N_{ref}}{N_X} \frac{A_X}{A_{ref}} \frac{M_X}{M_{ref}}$$

As described previously, A_X and A_{ref} refer to the integrated peak areas of the target and the (reference) solvent compounds, respectively. However, as opposed to the SPE-NMR where only the peak area ratio of the target to the reference is used for calculation, the Advanced SPE-NMR approach takes into account two more area integrals and ratios of such. Firstly, the ratios for the two solvent mixtures, established prior to the introducing of contaminants to the system, are established. Therefore, the following ratios have to be considered for estimating the measurement uncertainty:

$$\begin{aligned} r_1 &= \frac{a_1}{b_1} = \frac{A_{HMDSO,1}}{A_{CHCl_3,1}} \\ r_2 &= \frac{a_2}{b_2} = \frac{A_{HMDSO,2}}{A_{CHCl_3,2}} \end{aligned} \tag{A.1}$$

Upon introducing the contaminants into the system — be it decane and/or toluene as for measurement validation or crude oil/condensate/gas — the area integrals are derived anew over the same chemical

Measurement Uncertainty

shift range as before:

$$\frac{A_{c,1}}{A_{d,1}} \& \frac{A_{c,2}}{A_{d,2}} \quad (\text{A.2})$$

The uncertainty associated with the area ratio A_l/A_m can be determined via:

$$u(A_l/A_m) = \sqrt{\frac{\sum (x_k - \bar{x})^2}{n(n-1)}} \quad (\text{A.3})$$

Herein, x_k is the result for A_l/A_m of a single measurement and $\bar{x}$ is the average over n measurements.

To calculate the uncertainty of the molar mass M_j of a compound, the atoms contained in the chemical structure need to be considered taking into account their number N_i and the individual uncertainty of the respective atomic mass $u(i)$:

$$u(M_j) = \sqrt{\sum (N_i u(i))^2} \quad (\text{A.4})$$

The values of $u(i)$ are tabulated and are published by the Commission on Isotopic Abundances and Atomic Weights (CIAAW) [233].

Furthermore, the mass of the reference compound m_{ref} is deployed to determine the unknown mass of the target analyte in the relevant sample. Thus, in a first step, the uncertainty related to the concentration of a reference substance added to the solvent mixtures need to be established via:

$$u(c_{ref,solvent}) = c_{ref,solvent} \sqrt{\left(\frac{u(m_{ref})}{m_{ref}}\right)^2 + \left(\frac{u(V_{total})}{V_{total}}\right)^2} \quad (\text{A.5})$$

Equation A.5 is then incorporated when calculating the uncertainty of m_{ref} and c_{ref} (concentration) in the stock solution:

$$\begin{aligned} u(m_{ref,stock}) &= m_{ref,stock} \sqrt{\left(\frac{u(c_{ref,solvent})}{c_{ref,solvent}}\right)^2 + \left(\frac{u(V_{stock})}{V_{stock}}\right)^2} \\ u(c_{ref,stock}) &= c_{ref,stock} \sqrt{\left(\frac{u(m_{ref,stock})}{m_{ref,stock}}\right)^2 + \left(\frac{u(V_{stock})}{V_{stock}}\right)^2} \end{aligned} \quad (\text{A.6})$$

The stock solutions are subsequently diluted by adding the (uncontaminated) solvent mixtures to prepare the individual samples for measurement validation. This leads to the following equation for the estimation of uncertainty related to m_{ref} in the samples:

$$\begin{aligned} u(m_{ref,sample}) &= \left[m_{ref,stock}^2 \left(\left(\frac{u(c_{ref,stock})}{c_{ref,stock}} \right)^2 + \left(\frac{u(V_{stock})}{V_{stock}} \right)^2 \right) \right. \\ &\quad \left. + m_{ref,solvent}^2 \left(\left(\frac{u(c_{ref,solvent})}{c_{ref,solvent}} \right)^2 + \left(\frac{u(V_{solvent})}{V_{solvent}} \right)^2 \right) \right]^{\frac{1}{2}} \end{aligned} \quad (\text{A.7})$$

Ultimately, the individual contributions listed above can be combined to determine the measurement uncertainty associated with measurements deploying the Advanced SPE-NMR analysis to give:

$$u_c(m_x) = m_x \left(\left(\frac{u(A_{HMDSO,1}/A_{CHCl_3,1})}{A_{HMDSO,1}/A_{CHCl_3,1}} \right)^2 + \left(\frac{u(A_{HMDSO,2}/A_{CHCl_3,2})}{A_{HMDSO,2}/A_{CHCl_3,2}} \right)^2 + \left(\frac{u(A_{c,1}/A_{d,1})}{A_{c,1}/A_{d,1}} \right)^2 + \left(\frac{u(A_{c,2}/A_{d,2})}{A_{c,2}/A_{d,2}} \right)^2 + \left(\frac{u(M_x)}{M_x} \right)^2 + \left(\frac{u(M_{ref})}{M_{ref}} \right)^2 + \left(\frac{u(m_{ref})}{m_{ref}} \right)^2 \right)^{\frac{1}{2}} \quad (A.8)$$

Equation A.8 has to be calculated for the individual samples measured in order to accurately take into account the relevant target analyte, sample concentration and reference substance chosen for OiW concentration determination.

Sample Preparation

The uncertainty with respect to the formulation of the standard solutions needs to account for the uncertainties associated with the amount of contaminants initially weighed in as well as the volumes of solvent and stock solution used to prepare the individual samples. The uncertainty of the stock solution is estimated via:

$$u(c_{x,stock}) = c_{x,stock} \sqrt{\left(\frac{u(m_x)}{m_{x,stock}} \right)^2 + \left(\frac{u(V_{stock})}{V_{stock}} \right)^2} \quad (A.9)$$

Herein, m_x can refer to the sum of two contaminants, such as toluene and decane, as is the case for the samples relevant in the work presented here. The uncertainty of a sum m_x is calculated as:

$$u(m_x) = \sqrt{u(m_y)^2 + u(m_z)^2} \quad (A.10)$$

The individual validation samples are prepared by diluting the stock solution with the solvent mixtures; the corresponding uncertainty can be determined as follows:

$$u(c_{sample}) = c_{sample} \sqrt{\left(\frac{u(c_{stock})}{c_{stock}} \right)^2 + \left(\frac{u(V_{stock})}{V_{stock}} \right)^2 + \left(\frac{u(V_{sample})}{V_{sample}} \right)^2} \quad (A.11)$$

The uncertainty $u(V_{sample})$ refers to the combined uncertainty of the stock and solvent volume used to make up the specific sample volume.

Appendix B

SCT Automation - User Manual

B.1 General Information

This chapter provides some general information about the DickeBerta software and outlines the structure of this manual.

B.1.1 System Overview

DickeBerta is a LabVIEW program developed to automate the SPE-NMR procedure using the Self-contained Transportable (SCT) and enable user control of all involved steps. The software allows control of the individual steps during the SPE procedure, operation of the NMR spectrometer, it stores the NMR data and can perform post-processing and analysis of NMR spectra. DickeBerta needs the Spinsolve software as well as Matlab installed.

B.1.2 Organisation of the Manual

This user manual consists of six sections: General Information, System Summary, System Setup, Front Panel, Back Panel and Error Handling.

The General Information provides a brief overview of the software's purpose and describes the structure. In System Summary, a general overview of the software functions is provided. The hardware and software requirements are described as are the system configuration and behaviour of the system in case of any contingencies. The user will learn about how the system needs to be set up and the relevant settings in the System Setup section. The user interface is detailed in the Front Panel section. This is followed by an introduction into the block diagram, which represents the code of the program. Lastly, the section Error Handling describes how DickeBerta deals with any errors that occur during operations and provides some information regarding troubleshooting.

B.2 Setup

This chapter provides instructions on how to setup DickeBerta using LabVIEW. Note that it is not an installation guide for LabVIEW or any of the other required programs, such as Python or Matlab.

B.2.1 Software Requirements

In order to control the SCT for sample preparation and analysis with NMR, the LabVIEW application DickeBerta is used. The application requires LabVIEW 2016 fully licensed including the MathScript RT module.

Apart from LabVIEW, the following software is required to execute and use DickeBerta:

- Matlab (compatibility with LabVIEW needs to be checked)
- Python
- Spinsolve software (shipped with the spectrometer)

The user has to ensure that all software is installed properly and able to be used. Furthermore, the installation location of the executables of Python and the Spinsolve software need to be known (folder path).

B.2.2 Project Structure and Folder Setup

DickeBerta is a LabVIEW application consisting of one main VI (*DickeBerta.vi*) and multiple sub-VIs. The files required to run the application are organised within a root directory, "AutomatedSystem", and sorted into folders according to their functionality and purpose. Figure B.1 shows the folders contained in the root directory of the application. Within the root directory, all

Data	11/05/2018 2:34 PM	File folder	
Documentation	11/05/2018 12:03 PM	File folder	
Graphics	11/05/2018 12:03 PM	File folder	
LV Source	11/05/2018 2:53 PM	File folder	
Matlab	15/05/2018 11:18 AM	File folder	
Python	16/05/2018 9:20 AM	File folder	
ControllingSCT	15/05/2018 3:13 PM	LabVIEW Instrument	473 KB
SCT Control.aliases	15/05/2018 12:45 PM	ALIASES File	1 KB
SCT Control.lvps	15/05/2018 11:18 AM	LVLPS File	1 KB
SCT Control	15/05/2018 11:18 AM	LabVIEW Project	43 KB

Figure B.1 Folder structure within the application root directory *AutomatedSystem*

sub-VIs and controls that are part of and used in DickeBerta can be found in "LV Source" folder. This folder is further subdivided according to the specific purpose of the VIs.

All data generated by DickeBerta, such as configuration data or error logs, and the data from the NMR spectrometer are saved into the "Data" folder.

Furthermore, the "Matlab" folder contains all relevant m-files (scripts and functions) for NMR data processing and analysis and another folder, "Python", comprises the Python scripts essential for remote control of the Spinsolve NMR spectrometer.

Any specific documentation files can be found in the "Documentation" folder and any screenshots or photos of the program itself or associated with it are saved to "Graphics".

DickeBerta is located directly in the root directory and will always be loaded from there. Every sub-VI that it needs will be automatically accessed from within the program, the user does not have to open or load anything else to start the program.

B.3 Program Configuration and Setup

In a first step, the application folder "AutomatedSystem" shall be saved into a folder to which the user has read and write access. The folder structure within the root directory should not be changed as the program has dependencies regarding finding its sub-VIs and saving data to specific folders.

In order to use the DickeBerta with the Self-contained Transportable and online NMR spectrometer, Python, Matlab and the Spinsolve software are required alongside LabVIEW. Prior to running DickeBerta, some settings have to be adjusted within the specific software:

1. Spinsolve: The Spinsolve software has to be setup for remote control and a data folder selected, where the acquired spectra and parameters will be saved. Start the Spinsolve software and then navigate to software preferences. In the menu bar at the top left corner of the user interface, select "SYSTEM" and then "PREFS" as shown in Figure B.2a below. Within the software preferences, expand "DATA SETTINGS" and "REMOTE CONTROL". Set up the data path for the NMR data by choosing a folder for the base path (refer to Figure B.2b) according to your own preferences. It is recommended to select the folder "NMR data" in the "Data" folder within the root directory of the LabVIEW program. Any data generated by the Spinsolve software will automatically be stored to the base path according to year, month, date and time. The data path can be extended with variables and separators to construct folder names that are more comprehensible. Further to the data settings, remote control of the Spinsolve has to be enabled to run the software from DickeBerta. Under "REMOTE CONTROL" tick the enable checkbox and note the port specification. 1300 is the default setting and should not be changed.
2. Matlab: To be able to do data processing and analysis of the spectral data obtained through NMR measurement, a Matlab script is implemented in LabVIEW. This script calls various functions during execution, all of the required scripts and functions (m-files) are located in the "Matlab" folder. In the Matlab software itself, the search path or working directory has to be setup in order

Figure B.2 Spinsolve software user interface using (a) the menu bar to navigate to the system preferences and then (b) adjust the data settings and enable remote control.

to find and load the functions that are needed. Add the "Matlab" folder and the "NMR data" folder — in case a different folder was selected in the previous step (base path), this folder must be added instead of the "NMR data" folder — to Matlab's working directory.

3. LabVIEW: In LabVIEW, the folder where the NMR data is stored as well as the folder with all Matlab scripts and functions must be added to the search path. This is done by navigating to *Options* in the *Tools* drop-down menu of the menu bar. Select the category *Paths* and add the paths of the Matlab and data folder, respectively, to the VI search path. Furthermore, under the *MathScript* category, the path to the m-files must be added as well.

Further configuration settings have to be adjusted in DickeBerta itself. Open the program (double-click on DickeBerta.vi), but do not start/run the program yet. The front panel will automatically be loaded. Open the block diagram, either using the shortcut "Ctrl+E" or via the *Window* dropdown-list and clicking on "Show Block Diagram". This will open a separate window that contains the code of the program. In total, six while loops should be visible containing case or event structures. Navigate to the second while loop from the top, a flag in the top left corner indicates that this is the "MAIN LOOP". A case structure resides inside this loop, two settings have to be adjusted here:

- Select Case "Main-Init": Open *Spinsolve_start.vi* that is responsible for starting up the Spinsolve software upon initialisation of DickeBerta. This should be located to the left-hand side of the case and features the following icon: Show the block diagram, which consists of another case structure and some code. In here, the path of the Spinsolve executable (in the example shown, this is the path to Spinsolve All Users.exe) needs to be set according to the current folder where the software is located. Copy and paste the path — including the executable — into the path constant. It is possible to use both versions of the Spinsolve software (Spinsolve.exe and Spinsolve All Users.exe), the path and command line (pink border in Figure below) have to be modified according to the selected version.

- Select Case "Main-Shim": Open build_command_line.vi (refer to Figure below for the icon) and then its block diagram. In here, the string constant (pink frame, highlighted in Figure) needs to be changed to reflect the path to the python executable. Do not remove the initial letters "cmd /c" of the string, only substitute the path "C:\...". Again, it is essential that the path contains the executable as demonstrated in Figure.
- Front Panel: On the front panel (user interface of DickeBerta) on the right-hand side under "Error log", the folder where potential error logs shall be saved needs to be set. By default, this is ...AutomatedSystem\Data\Error log.

B.4 Using the Program

B.4.1 Startup

After confirming that the required set-up steps as per Chapter B.2 are performed, DickeBerta can be opened in LabVIEW. The program can be loaded by either double-clicking on the main VI DickeBerta.vi or by first opening the project SCTControl and then starting the main VI via the project explorer. This loads the front panel of the program, which is essentially the user interface. The front panel and how to use it is described in more detail in Section B.4.2 below.

The user has to make sure that the Spinsolve and the control box (shown in Figure B.4) are connected to the laptop via USB. Furthermore, it is required to check that the components of the SCT are connected to the correct port. Apart from the Spinsolve, all instruments should be powered off at this stage. Subsequently, the user can start the program by hitting the run button found on the LabVIEW toolbar as demonstrated in Figure B.3.

Figure B.3 Run button to start the LabVIEW application located at the top toolbar.

Once the program has been started, the instruments can be powered up at the power sockets. Next, the control box, which is shown in Figure B.4, can be switched on with the black button on the front. The control box must only be switched on once the LabVIEW program has been started. This is essential for preallocation of the valve positions with the last statuses saved to a configuration file. In the case that power is supplied to the valves without providing positions, the valves will go to their default states. This is generally not desired as it might cause liquid movement in the tubing.

Figure B.4 Control Box for the SCT with the on/off switch highlighted. The box must only be turned on after the LabVIEW program DickeBerta has been started.

Once DickeBerta runs and power is supplied to the equipment, the user can operate the SCT and start measurements. The following section provides instructions on how to use DickeBerta to control the SCT.

B.4.2 Front Panel

The front panel of a LabVIEW program is essentially the graphical user interface which the user predominantly uses while running the program or application. The front panel of DickeBerta has the required functionality to control the components of the SCT, start and stop NMR measurements and perform data processing and analysis. Furthermore, it is provided with indicators to inform the user about the status of the components / controls and as a means to confirm the current operation.

The main object on the front panel is a tab control (refer to Figure B.5 below), where each tab implements specific functionality regarding the components of the SCT that the user controls. The individual tabs, their purpose and instructions on how to use the controls is described in more detail below.

To the left-hand side of the front panel, indicators for the digital output lines can be seen. The mechanical components of the SCT are controlled via logic levels that operate on a digital signal. For this system, two logic levels high and low are used to switch components on and off or open and close with respect to the valves. Via LabVIEW, the user provides the required digital signal to trigger a change in a logic level and thus controlling which component to turn on or off. The indicators for the digital output lines are for monitoring purposes only, they cannot be used in terms of control.

Shutdown of the program should always be performed via the shutdown button on the right-hand side of the front panel. Refer to a more detailed description of the procedure below.

The Error log section located below the shutdown button on the right-hand side is for documentation purposes. The user selects where error log files shall be saved by clicking on the folder button. A string indicator displays any error messages as they occur.

Figure B.5 User interface (front panel) of DickeBerta.

The following sections describe each tab of the tab control in more detail.

B.4.3 Motor Control

The *Motor Control* tab provides the functionality required to move any of the three motors — x = horizontal, y = vertical bottom and z = vertical top — via the controls in the top part of the tab as shown in Figure B.6. Furthermore, the tab displays indicators with respect to the position of each motor (bottom part in Figure B.6).

Figure B.6 *Motor Control* tab on DickeBerta's front panel. Movement of the three motors is facilitated and indicators show the current positioning.

Common Motor Functionality

Start / Stop Motor

The *Start / Stop Motor* button is used to initiate or stop motor movement. When one of the motors is moving, all other controls on the *Motor Control* tab are disabled and greyed out to prevent sudden changes that potentially disrupt normal operation or damage the motors or control box. This is also true should the *Move Home* button have been used to initiate motor movement.

Move Home

The *Move Home* button automatically moves the selected motor backwards until it reaches its home position unless the user suspends the motion by pressing the *Start / Stop Motor* button to stop the motor. The home position is determined with the help of a limit switch. As soon as the motor hits the limit switch, movement is reversed (hence will go forwards) for a predetermined number of rotations and then stops. Once the motor is stopped in its home position, the relevant indicator under *Home?* will change colour to show orange and read "At Home" as can be seen in Figure B.7 below for the bottom vertical motor.

Figure B.7 Example of the home position indicator for motor y (vertical bottom) showing that it is in the home position or "At Home".

Motor Selection

The drop-down list *Motor Selection* allows the user to select one of the three motors. This can be done via clicking onto the currently selected motor, which causes the list to unfold and the selection can be changed. Or the increment / decrement button on the left-hand side can be used to switch between the three motors x, y and z.

Direction

The *Direction* drop-down list can be used in the same manner as the *Motor Selection* list to switch between forward or backward direction of the motors. Note that this control is disabled when the position control (see below) for the horizontal motor is enabled.

End-of-Travel Limit Switch

The three linear motion slides have end-of-travel (EOT) control by means of a limit switch. The program will display a pop-up window as soon as one of the end-of-travel limit switches is hit to ask if the motor should move to home position. The status will be saved to the folder *Configuration Data* in form of a txt file.

Shutdown Functionality

When the program is shut down and any of the feedback lines indicate that a load cell and / or limit switch is activated, the statuses will automatically be saved and reloaded upon the next startup. Furthermore, should the program be shutdown after a limit switch has been hit without reset, the relevant motor and direction are saved to a configuration file. This enables resetting the limit switch when the program is run the next time.

Individual Motor Functionality

The following provides instructions and details pertaining to the horizontal and vertical motors, respectively.

(i) Horizontal (x):

- Movement of the horizontal movement is only allowed when both vertical motors are in their home position. A pop-up window will inform the user if the vertical motors are not at home and movement is inhibited.
- Movement can be done manually by selecting the direction — *Forwards* or *Backwards* — from the *Direction* drop-down list and hitting the start button, *Start / Stop Motor*.
- A toggle switch is available when the horizontal motor is selected. This switch enables a position slide control. Using the slide control, the user can select a cartridge position and then hit the *Start / Stop Motor* button to start the motor. The program automatically determines which direction to choose and will stop in the correct position. This function can only be used when the motor is at a known cartridge position and cannot be combined with manual motor movement.
- The home position of the motor corresponds to position "0" on the slide control.

(ii) Vertical (y and z):

- The two vertical motors have the same functionality.

- Movement is initiated by selecting the motor and direction via the drop-down lists, then hitting the start button (*Start / Stop Motor*). Backwards movement can also be started by using the *Move Home* button.
- The vertical motors are used to connect / disconnect the cartridges. Moving any of the two vertical motors forward will move the cartridge connector towards the cartridge. It is essential that the cartridge is in the correct position to enable smooth connection. If the connector and cartridge cap are not aligned, damage to the cap and / or the connector can occur as they make contact, e.g. the point of the needle (on the connector) might hit the edge of the cartridge cap and consequently be bent. Load cells are installed as part of both top and bottom connectors to determine when a connection is established. The load cell measures the force exerted onto the cartridge cap with the connector. Once a pre-set limit is reached, a hardware stop is triggered and a digital signal sent to the program which subsequently resets the motor on the front panel. The load cell indicator will light up as is shown in Figure B.8 below.
- Once a load cell is active, hence a connection is made, forwards movement of that motor is inhibited. The user is informed via a pop-up window should the start button with forwards movement be hit.

Figure B.8 Example of current position or status of the motors showing via the indicators on the Motor Control tab on the front panel.

B.4.4 Valve Control

The power to the valves is always on. Valve positions are saved to a configuration file when the system is shut down and will automatically pre-load upon starting the program. Therefore, it is essential that DickeBerta is started before the control box is switched on (see above B.4.1) in order to prevent the valves to return to their default position (A) as soon as power is supplied.

Spinsolve Valve

The valve at the exit of the Spinsolve is normally open. When a NMR spectrum is to be measured, this two-way valve shall be closed by pressing the *Spinsolve valve* button. Figure B.9 shows the colour and text change of the button as the valve is closed.

Figure B.9 Closing the Spinsolve valve for NMR measurement.

Opening of the valve upon completion of a measurement is essential to avoid overheating. The valve is a solenoid-valve, hence uses a electric current supplied to a solenoid to induce mechanical movement in a plunger, that closes off the fluid path. Therefore, the valve must not be left in the closed and thus energised state longer than a couple of minutes .

Three-way Valves

The valves that are used to control the fluid flow paths in the automated system are electrically actuated, three-way ball valves. They are used to choose the correct flow path for the SPE stages and NMR measurement. The valves have a L-port configuration providing two positions, referred to as A and B, as schematically shown in Figure B.10.

Figure B.10 L-port configuration of three-way ball valves showing positions A and B with a common outlet C.

Using the horizontal switches, *Valve Position*, on Valve Control tab of the front panel (shown below in Figure B.11), the user can change the valve position. Position A is marked in turquoise, position B in royal blue.

Figure B.11 Valve control tab on the front panel of DickeBerta. The Spinsolve valve is a two-way valve, normally open; the button can be used to close the valve. The other valves are three-way valves with L-configuration.

Valves are switched following the standard operating procedure. Approximately 10 to 15 seconds are required for a full turn and engaging in the new position. Switching of more than two valves at once should be avoided as this might cause pressure build-up in the system.

B.4.5 Sample and Solvent Pump

The two pumps are operated via the *Sample Pump* and *Solvent Pump* tabs shown in Figure B.12.

Figure B.12 Control of the two pumps for (a) sample loading and (b) solvent elution on the front panel of DickeBerta.

Both pump controls work in the same way. The user specifies the volume of liquid to pump and hits the start/stop button. Due to the position of the first valve, which is used to switch between sample and solvent, the section of tubing between the pumps and this valve becomes dead volume. Therefore, in order to achieve the desired throughput, the volume to pump has to be set to the actual value plus 5 ml.

The pump automatically stops when the set volume has been pumped or can be stopped manually by pressing the start / stop button. An indicator below the tab control displays the volume delivered by the currently active pump. Only one pump can run at a time, the MFC and motors are also disabled when one pump is active.

Note that it is crucial to check the correct valve positions to prevent pumping liquid against a closed valve. The pumps have an emergency shut-off (hardware stop) should the pressure at the outlet reach or exceed 100 bar.

B.4.6 MFC Control

The mass flow controller (MFC) is operated in a similar way to the pumps. Figure B.13 shows the *MFC Control (Air Flush)* tab that provides the functionality to flush the system with compressed air.

Figure B.13 MFC control tab on the front panel of DickeBerta. The duration of the air flush is set and compressed air applied to the system using the start/stop button.

The user sets the desired duration of the flush and activates the MFC by pressing the *On / Off* MFC button. The MFC consists of a mass flow meter and control valve, thus activating the MFC allows the compressed air, applied to the inlet of the MFC, to pass through. The MFC is set to deliver the pressure on the inlet. The MFC closes when the timer has run out or the on / off button is pressed.

B.4.7 NMR Measurement

The *NMR Measurement* tab enables the user to perform measurements with the Spinsolve NMR spectrometer and the magnet can be shimmed. In Figure B.14, the tab and contained controls are shown.

Figure B.14 Tab control on the front panel that enables operation of the Spinsolve NMR spectrometer. Three different types of shimming as well as pulse-and-collect sequences to obtain frequency domain spectra with an adjustable number of scans can be run.

The magnet is shimmed using the controls found on the left-hand side of the tab under *SHIMMING*. Via the drop-down list, the user can select the shim protocol to run — *Checkshim*, *Quickshim* or *Powershim* — and start the shim with the green *Start* button. Similarly, a spectrum is measured by defining the number of scans and starting the measurement with the orange *Start* button. A measurement or shim is aborted using the red *ABORT* button located below the two start buttons.

Whenever a measurement is started, the other controls are disabled to prevent overloading the communication port of the Spinsolve with messages. The *ABORT* button is always enabled to allow cancellation of the current measurement. On the right-hand side of the tab, indicators provide information about the measurement upon completion. The top indicator displays the measurement that has been completed, i.e. Checkshim, Quickshim, Powershim or Spectrum, or it shows "N / A" in case of measurement abortion or when no measurement has been run so far. The boolean indicator *Successful?* informs the user about the successful (green) or unsuccessful (red) measurement completion. With regards to shimming the magnet, successful means that the achieved linewidth at half height is less than 1 Hz and the system is ready. Note that spectra can be measured with a linewidth greater than 1 Hz as well. Under *Details*, the user can obtain information about the measurement. In the case of a spectrum, the time of the measurement is displayed. For any shim protocol, the achieved linewidth and recommendations how to proceed are provided. An example message is shown in Figure B.15 below. Should an error occur during measurement, this will also be detailed here.

Figure B.15 Example of details about the measurement just completed provided to the user. In this case, a shim was run and the achieved linewidth at half height (linewidth 50%) is greater than 1 Hz, therefore a Quickshim is recommended to the user.

The number of scans defined for the measurement of a frequency domain ^1H NMR spectrum must be a number to the power of two. However, a default value will be supplied to the Spinsolve should the user enter a number that is not to the power of two. The default number of scans is 8 resulting in a measurement time of 2 minutes. The rest of the parameters for the spectrum measurement are pre-set as follows:

- Acquisition time: 6.4 s
- Repetition time: 15 s
- Pulse angle: 90

If the user wished to change these, the Python script *Spectrum* can be adapted to incorporate the changes.

Once the NMR spectrum is recorded, a user dialog, see Figure B.16 (a), pops up asking the user to provide information about the measurement.

(a)

(b)

Figure B.16 (a) User dialog to save data related to the NMR measurement performed. The information — SPE number, solvent volume, sample volume and any additional comments — is then saved to a text file including the end time of the NMR measurement. A typical text file is shown in (b).

The user can assign a number to the SPE procedure performed, record the sample and elution volumes and add any comments/observations regarding the measurement. The time at which the NMR measurement was completed is added automatically. The data provided is subsequently stored in form of a text file such as the one shown in Figure B.16 (b) that is named with the current date. Subsequent measurement information is added to the bottom of the file.

B.4.8 Data Analysis

Post-processing and analysis of the measured NMR spectra is done via the *Data Analysis* tab which can be seen below in Figure B.17.

Figure B.17 Data analysis tab on the front panel of DickeBerta providing functionalities for data analysis and displaying the generated output for the user.

The bottom half of the tab enables user input. Default values will be preallocated to the *Produced Water Volume [ml]*, *Density Crude Oil [g/ml]*, *Solvent Volume [ml]* and *Concentration CHCl₃ in Solvent [%]*. To obtain accurate results for the measured concentration of oil in water, it is essential that the user provides the sample and solvent data according to the measurement performed. A data file must be loaded via the *File location* control located under *Sample Data* (refer to Figure B.17). An error occurs if no file is selected for analysis. If the solvent is recycled, a baseline measurement is conducted before eluting the cartridge to determine the contamination in the solvent. In this case, the user must tick the checkbox *Baseline Measurement?* and load the relevant data to ensure that the initial oil content in the solvent is taken into account when the program calculates the oil-in-water concentration.

After all input has been provided as required, the user starts the data analysis with the orange *Analyse* button. The button will be greyed out as long as the analysis, consisting of post-processing the data obtained through NMR measurement and evaluation of the spectrum, is processed. Once completed, a value will be displayed in the *Oil-in-Water [mg/L]* indicator. For visualisation and validation, the frequency domain spectrum of the relevant sample is plotted in the graph indicator on the right-hand side of the tab (amplitude versus chemical shift). Should the spectrum appear skewed/distorted, the user can change the *Baseline parameter* — the control is located directly underneath the *Analyse* button. By default, the value can only vary in 0.5 increments between 1 and 10, and should only be changed if the spectrum is visibly distorted. This is usually the case if interferences, such as a water peak, are present.

Note that the data processing is performed in the background with Matlab using a Matlab script and functions. Should an error occur, the user is advised to check data input and output to and from the script as well as the search paths selected both in LabVIEW and in Matlab.

B.4.9 Shutdown

Shutdown of DickeBerta must be performed using the *Shutdown* button to the right-hand side of the front panel. The button is shown in Figure B.18 below.

(a)

(b)

Figure B.18 (a) Shutdown button to stop the LabVIEW Program DickeBerta in an orderly process and (b) invoked user dialog for confirmation that shutdown shall proceed.

The *Shutdown* button initiates the correct shutdown of the program during which configuration files are generated, all loops are gracefully exited, the main VI is stopped and leaves the memory. When the *Shutdown* button is pressed, a window pops up asking the user to confirm the shutdown. If the action is cancelled, normal operation can proceed.

The user should avoid using the *Abort Execution* function found in the runtime menu of the LabVIEW interface. The button is highlighted in Figure B.19.

Figure B.19 Stop button (*Abort Execution* in the LabVIEW runtime menu located at the left-hand side of the task bar.

Furthermore, shutting down the application by closing the window (red X top right) is inhibited. A user dialog, shown in Figure B.20, opens with the information that DickeBerta is still running.

Figure B.20 User dialog preventing that the window is closed while the application is still running and has not been shut down properly.

The user has to confirm that the message is read, initiate orderly shutdown via the *Shutdown* button and can then close the window.

B.5 Block Diagram

The block diagram is essentially the program code implementing the functionality that is required to execute the desired tasks. DickeBerta is structured as a multi-loop, enqueued state machine with an event structure that captures user input or other events generated from within the program. The other loops are essentially responsible for executing the demanded actions. In the following, the various loops are described at a high-level of detail. The user is referred to the context help if information about the subVIs that are used/called from the main VI, DickeBerta. Should more information with

regards to programming concepts, instructions to use LabVIEW and LabVIEW VIs, functions, palettes, menus, and tools be required, the user is referred to the LabVIEW help or the National Instruments community (<https://forums.ni.com/>).

B.5.1 Event Structure

The *Event Handling Loop*, shown in Figure B.21 below, is used to capture user events on the front panel as well as events that are generated from within the program.

Figure B.21 Event handling loop on the block diagram of DickeBerta. This loop is used to capture user events as well as events generated within the program.

Every active control on the front panel is linked to an event and addresses a specific case within the event handling loop. Should a control on the front panel be used, the respective event is triggered and the relevant code contained in the case executed. This in turn enqueues a state for the *Main Loop*, which can be regarded as the heart of the program.

In addition to events created on the front panel, the program itself triggers events in certain cases. For example, if one of the motors hits an EOT limit switch, an event is triggered that stops the motor and asks the user for input. Other events generated by the program itself kick off actions automatically, such as the home position reset after a motor has hit the home position limit switch.

In the case that no event happens, the event structure goes into the timeout event case. Herein, the indicators on the user interface of DickeBerta are updated to reflect the current status. This includes the load cell and limit switch indicator, the cartridge position, the volume pumped by either of the two pumps and the home position indicators of the motors. A value of 200 (in ms) is wired to the timeout event terminal, meaning that the timeout will occur every 200 ms if no event is captured.

B.5.2 Main Loop

As noted above, the main loop is the heart of the program. It either directly executes tasks or directs the sub-loops to perform certain actions according to the events captured in the event loop. Figure

B.22 below displays the main loop showing the default case where the main loop is idle, hence waiting on input.

Figure B.22 Main loop on the block diagram of DickeBerta. The states in this loop are triggered by the event structure and direct the relevant action in the other loops.

For tasks that requires a digital output, for example movement of the motors or switching any of the valves, the main loop directs the *Digital Output Loop* to execute the code in the corresponding case. At the same time, the *Feedback Loop* and *Counter Input Loop* are also controlled to switch into the required state. The tasks of data analysis and remote control of the Spinsolve are executed from within LabVIEW, hence without a digital output signal, and are dealt with directly in the main loop.

The main loop has an idle state which has a similar functionality as the timeout event of the event loop. If any of the motors is running, the load cell and limit switch feedback is monitored to trigger a user event should a signal be received. Furthermore, if the horizontal motor is moving in combination with the cartridge position slider, the idle state triggers a user event to stop the motor when the correct position is reached. Provided that no motor is moving, the current pumping volumes are monitored and the current SPE step determined according to valve positions. These are stored in so called action engines that can be read elsewhere in the program, for example during the timeout event in order to update the user interface. The idle state also executes a Python script in the background that checks if a measurement with the Spinsolve has been completed. The Python script looks for a xml file that is automatically generated upon measurement completion. As soon as a file is found, the contained information (successful or not plus details provided by the spectrometer) is extracted and displayed on the NMR Measurement tab on the user interface.

Upon start-up of DickeBerta, the main loop automatically executes an initiation case which starts the Spinsolve software, initiates the digital tasks for instrument control and loads the default control states as well as the last valve and motor position states. As soon as the user requests shutdown of DickeBerta, the shutdown case of the main loop is executed. This case ensures that the program is stopped in an orderly manner saving the relevant configuration data and closing the Spinsolve software.

B.5.3 Digital Output Loop

The *Digital Output Loop* executes any tasks that require the transmission of a digital signal to any of the instruments. In the default case — "idle" which is shown below in Figure B.23 — simply writes the current values of digital high or low to the action engine of the digital output lines. This is used for display on the user interface to inform the user of the current status (the action engine is read in the timeout case of the event loop).

Figure B.23 Digital output loop on the block diagram of DickeBerta used to generate digital output tasks that control the components of the SCT.

The digital output loop is exclusively in charge of setting the digital lines to the correct value in order to start/stop the pumps, motors and mass flow controller and switch the valves to the desired position. The instruction to execute the specific case is generated in the main loop.

B.5.4 Feedback Loop

The *Feedback Loop* reads the three digital input lines available to send communication from the instruments to the computer. In Figure B.24, the case concerned with reading the feedback lines is shown.

The limit switches and load cells trigger cessation of any motor movement, this is implemented as a hardware stop to avoid any time delays that might be induced by slow communication or software failure. But information about the hardware stop is sent to the computer via a digital signal and this signal is read in the feedback loop so that the correct action is taken in the program. Only a limited number of input lines is available with the deployed LabVIEW interface, therefore the exact origin of the digital signal is determined programmatically (in the idle state of the main loop). The status of the digital input lines is cached in another action engine, that is monitored in the main loop for any changes. The feedback loop does not have any other functionality.

Figure B.24 Feedback output loop on the block diagram of DickeBerta that samples the input from the digital input (feedback) lines of the SCT.

B.5.5 Counter Input Loop

The LabVIEW interface deployed for this experimental setup provides one digital counter input line to enable counting of the rising or falling edges of a digital signal. A counter input can be used for timing and triggering dependent tasks. In DickeBerta, the counter input is used to control the pump volume (timing on the basis of a constant flow rate), the horizontal motor position and the flushing with compressed air. The main loop instructs the counter loop to reset and start counting upon starting a task that requires timing. Again, an action engine is used that converts the counter signal into a time and caches the value to be subsequently read somewhere else in the program. An image of the counter input loop is provide in Figure B.25.

Figure B.25 Counter input loop on the block diagram of DickeBerta that enables to use the counter input as a timer.

Appendix C

Python Scripts for Remote Control of the Spinsolve

Python scripts that enable remote control of the Spinsolve NMR spectrometer to shim the magnet, perform pulse-and-collect measurements and abort a shim or measurement. The scripts are called from LabVIEW.

Once a measurement has been successfully completed, a xml file is created that contains the last message sent from the Spinsolve. The script "search.py" is called in the idle state of the LabVIEW program and looks for this xml file. As soon as it is found, LabVIEW extracts the contained information and displays it to the user interface.

C.1 Checkshim

```
# Script to initiate a Checkshim with the Spinsolve
# receives the messages from the Spinsolve and saves the last message
# into the "results" xml file in the folder, where the script is
  located
import sys
import os
import socket
import time
import html
import re

# gets the host (IP) address of the computer
HOST = socket.gethostbyname(socket.gethostname())
PORT = 13000 # Default port
```

```
# establishes a socket
s = socket.socket(socket.AF_INET, socket.SOCK_STREAM)
# connects to the socket using IP and port
s.connect((HOST,PORT))
# constructs the xml based message for the Spinsolve to start a
  Checkshim
message = "<Message>\r\n"
message += " <CheckShimRequest/>\r\n"
message += "</Message>\r\n"
#sends the message to the socket (Spinsolve)
s.send(message.encode())
# initialises the response message
response=""
# sets the timeout - script waits on messages, when no more messages
# are received the timeout occurs (Spinsolve is done)
s.settimeout(2)
# as long as messages are received, these are collected from the
  buffer

try:
    while True:
        time.sleep(2)
        chunk = s.recv(8192)
        if chunk:
            response += chunk.decode().replace('\r\n','')
# when an error occurs, the timeout is set to 0 to close the
  connection;
# the error message is saved into the spectrum.Message xml file
except socket.error as msg:
    s.settimeout(None)

# when the measurement is completed, the last message received from
  the
# Spinsolve is saved into a xml file; searches for the last message
  using a
# regular expression
p = re.compile('<CheckShimResponse[\s\S]*?</CheckShimResponse>')
m = p.findall(response)[-1]
# unescape deals with special characters and includes them as symbols
results = html.unescape(m)
# removes linebreaks
results = results.replace('\n', '')
```

```
# a xml file is created as soon as the measurement is done in the
    location
# (folder) where the script is, xml file contains the last message
    received
location=os.path.realpath(os.path.join(os.getcwd(),
                                         os.path.dirname(sys.argv[0])))
with open(os.path.join(location,'results.xml'), "w") as f:
    f.write(results)

# closes the connection once the timeout occurs and the files are
    saved
s.close()
```

C.2 Quickshim

```
# Script to start a Quickshim with the Spinsolve
import sys
import os
import socket
import time
import html
import re

HOST = socket.gethostname(socket.gethostname()) # Computer IP
    address
PORT = 13000 # Default port
print('Connect to ' + HOST + ':' + str(PORT))
s = socket.socket(socket.AF_INET, socket.SOCK_STREAM) # establish
    socket
s.connect((HOST, PORT)) # connect to the socket
# construct the xml message to be sent to the Spinsolve
message = "<Message>\r\n"
message += " <QuickShimRequest/>\r\n"
message += "</Message>\r\n"

# Sent the xml message
s.send(message.encode())
# initiate the response message string
response=""
s.settimeout(2)
try:
    while True:
        time.sleep(2)
```



```
        chunk = s.recv(8192)
    if chunk:
        response += chunk.decode().replace('\r\n','')
# when an error occurs, the timeout is set to 0 to close the
    connection;
# the error message is saved into the spectrum.Message xml file
except socket.error as msg:
    s.settimeout(None)

# when the measurement is completed, the last message received from
    the
# Spinsolve are saved into a xml file
p = re.compile('<QuickShimResponse[\s\S]*?</QuickShimResponse>')
m = p.search(response)
results = html.unescape(m.group())
results = results.replace('\n', '')

# a txt file is created as soon as the measurement is done
location=os.path.realpath(os.path.join(os.getcwd(),
                                         os.path.dirname(sys.argv[0])))
with open(os.path.join(location,'results.xml'), "w") as f:
    f.write(results)

# closes the connection once the timeout occurs and the files are
    saved
s.close()
```

C.3 Powershim

```
# Script to initiate a Powershim with the Spinsolve
import sys
import os
import socket
import time
import html
import re

HOST = socket.gethostbyname(socket.gethostname()) # Computer IP
    address
PORT = 13000 # Default port

s = socket.socket(socket.AF_INET, socket.SOCK_STREAM)
s.connect((HOST, PORT))
```

```

message = "<Message>\r\n"
message += " <PowerShimRequest/>\r\n"
message += "</Message>\r\n"
s.send(message.encode())
response=""
s.settimeout(2)
try:
    while True:
        time.sleep(2)
        chunk = s.recv(8192)
        if chunk:
            response += chunk.decode().replace('\r\n','')
# when an error occurs, the timeout is set to 0 to close the
    connection;
# the error message is saved into the spectrum.Message xml file
except socket.error as msg:
    s.settimeout(None)

# when the measurement is completed, the last message received from
    the
# Spinsolve are saved into a xml file
p = re.compile('<PowerShimResponse[\s\S]*?</PowerShimResponse>')
m = p.search(response)
results = html.unescape(m.group())
results = results.replace('\n', '')

# a txt file is created as soon as the measurement is done
location=os.path.realpath(os.path.join(os.getcwd(),
    os.path.dirname(sys.argv[0])))
with open(os.path.join(location,'results.xml'), "w") as f:
    f.write(results)

# closes the connection once the timeout occurs and the files are
    saved
s.close()

```

C.4 Spectrum - 1D Extended+

```

# Script for running a pulse-and-collect measurement with the
    Spinsolve
# The script receives the number of scans from the user interface of
    the

```

Python Scripts for Remote Control of the Spinsolve

```
# LabVIEW program or uses a default value; all other parameters are  
    defined  
# script (acquisition time, pulse angle, repetition time)
```

```

message += "<Start protocol='1D EXTENDED+'>\r\n"
message += "<Option name='Number' value='"+noscan+"' />\r\n" # set
        value
message += "<Option name='AcquisitionTime' value='6.4' />\r\n"
message += "<Option name='RepetitionTime' value='15' />\r\n"
message += "<Option name='PulseAngle' value='90' />\r\n"
message += "</Start>\r\n"
message += "</Message>\r\n"

# sends the message to the Spinsolve as a xml file
s.send(message.encode())

# initiate the response message string
response = ""

# set the timeout for waiting on a message from the Spinsolve
# timeout is used to determine when the measurement is done
# (no more messages will be received)
s.settimeout(2)

# as long as messages are still coming in, they are received,
# decoded and added to the response string
try:
    while True:
        time.sleep(2)
        chunk = s.recv(8192)
        if chunk:
            response += chunk.decode().replace('\r\n', '')
            # appends the messages received from the Spinsolve
            # to the response string and removes the line breaks

# when an error occurs, the timeout is set to 0 to close the
    connection;
# the error message is saved into the spectrum.Message xml file
except socket.error as msg:
    s.settimeout(None)

# when the measurement is completed, the last message received from
    the
# Spinsolve are saved into a xml file
p = re.compile('<StatusNotification[\s\S]*?</StatusNotification>')
m = p.findall(response)[-1]
results = html.unescape(m)
results = results.replace('\n', '')

```

```
# a txt file is created as soon as the measurement is done
location=os.path.realpath(os.path.join(os.getcwd(),
                                         os.path.dirname(sys.argv[0])))
with open(os.path.join(location,'results.xml'), "w") as f:
    f.write(results)

# closes the connection once the timeout occurs and the files are
  saved
s.close()
```

C.5 Abort

```
# Script that aborts the current NMR measurement (shim or spectrum),
# receives the messages from the Spinsolve and saves the last message
# into the "results" xm file in the folder, where the script is
  located
import sys
import os
import socket
import time
import html
import re

# gets the host (IP) address of the computer
HOST = socket.gethostbyname(socket.gethostname())
PORT = 13000 # Default port

# establishes a socket
s = socket.socket(socket.AF_INET, socket.SOCK_STREAM)
# connects to the socket using IP and port
s.connect((HOST, PORT))
# constructs the xml based message for the Spinsolve to abort the
  measurement
message = "<Message>\r\n"
message += " <Abort/>\r\n"
message += "</Message>\r\n"

#sends the message to the socket (Spinsolve)
s.send(message.encode())
# initialises the response message
response=""
```

```

# sets the timeout - script waits on messages, when no more messages
    are
# received the timeout occurs (Spinsolve is done, no more messages
    are sent)
s.settimeout(2)
# as long as messages are received, these are collected from the
    buffer
try:
    while True:
        time.sleep(2)
        chunk = s.recv(8192)
        if chunk:
            response += chunk.decode().replace('\r\n','')
# when an error occurs, the timeout is set to 0 to close the
    connection;
# the error message is saved into the spectrum.Message xml file
except socket.error as msg:
    s.settimeout(None)

# when the measurement is completed, the last message received from
    the
# Spinsolve is saved into a xml file; searches for the last message
    using a
# regular expression
p = re.compile('<StatusNotification[\s\S]*?</StatusNotification>')
m = p.findall(response)[-1]
# unescape deals with special characters and includes them as symbols
results = html.unescape(m)
# removes linebreaks
results = results.replace('\n', '')

# a xml file is created as soon as the measurement is done in the
# location (folder) where the script is, xml file contains the last
# message received
location=os.path.realpath(os.path.join(os.getcwd(),
                                         os.path.dirname(sys.argv[0])))
with open(os.path.join(location,'results.xml'), "w") as f:
    f.write(results)

# closes the connection once the timeout occurs (no more messages
    received)
# and the files are saved
s.close()

```

C.6 Search

```
# Script that is regularly executed via LabVIEW to check if the
# results.xml
# file exists - the results.xml file is created upon successful
# completion of
# a shim or a measurement with the Spinsolve and contains information
# about
# the measurement
import sys
import os
import socket
import time
import os.path
# get path to current working directory
location=os.path.realpath(os.path.join(os.getcwd(), os.path.dirname(
    sys.argv[0])))
# in case the file exists, the output is 0, otherwise 1; if 0,
# LabVIEW reads the
# xml file and extracts the relevant information
if os.path.isfile(os.path.join(location,'results.xml')):
    print('0')
else:
    print('1')
```

Appendix D

Matlab Algorithm for Spinsolve Data Processing

Matlab source code for data processing of data obtained from pulse-and-collect measurements with the Spinsolve NMR spectrometer using the Spinsolve software. The main script is directly implemented in LabVIEW and calls the various functions.

D.1 Main Script

```
% Script for importing and processing the raw data created with
    Spinsolve
% (data.1d)
% The time domain data is fourier transformed, then baseline
    corrected and
% phase. Subsequently, the chemical shift scale is established and
    from the
% final spectrum, the oil concentration is extracted

userpath('C:\Users\SCT\Documents\LabVIEW_Programs\AutomatedSystem\
    Matlab');
fid = fopen(find_file); % opens the binary data file that
% contains a header along with the time data and both real and
    imaginary
% components of the signal
raw_data=fread(fid,Inf,'float',0,'l'); %reads the data file into an
    array
% called raw_data
```


Matlab Algorithm for Spinsolve Data Processing

```
fclose(fid); % closes the data file

% time data with the signal - real and imaginary parts are combined
% in a
% complex number - into one matrix, first column is time, second is
% signal
[fid_matrix, N, dt, df, f]=read_data1D(raw_data);

% fourier transformation of the time domain data to get a frequency
% domain
% spectrum (spectrum_raw) with the zero frequency component shifted
% to the
% centre of the spectrum, Yreal is a vector containing the real Y
% data of
% the spectrum, spectrum_shifted has the maximum peak shifted to 0 Hz
[Yreal, Yshift_0freq, f_shift_max, spectrum_shifted] = fid_transform
(...
                                fid_matrix, N
                                , f);

% apply baselinecorrection to the spectrum, output is a matrix with
% first
% column frequency and second column baseline corrected complex
% spectrum
% also outputs separate matrices containing the peak and baseline
% points
% respectively (with the associated frequencies) and the minimum
% noise
% value; k is an input parameter provided by the user (dependend on
% the
% spectrum, default = 3)
[peaks,baseline_points,noise,spec_basecorrect]=extractBase(...
                                spectrum_shifted
                                ,200,64,k);

% extract the data of the detected peaks - index, frequency,
% amplitude
pks = extractPeaks(spec_basecorrect, noise, f_shift_max);

% extract the tail points of each peak - start index and end index
```

```
tail_info = extractTails(f_shift_max, df, peaks, pks, size(pks,1));

PH_init = [0,0]; % intialize phase angles - 0 means no phase
               correction
% minimize the objective function by changing PH
PH_coarse = fminsearch2(@(PH_init) objective_function(4,...
               spec_basecorrect(:,2), PH_init, tail_info), PH_init);
% phase the spectrum with the phasing parameters obtained from coarse
% tuning
phased_coarse=phase(spec_basecorrect,PH_coarse);

% fine tuning of the spectrum by calculating the penalty function
               with
% the function fine_tune and minimizing the value
PH_fine = fminsearch2(@(PH_course) fine_tune(phased_coarse,tail_info
               ,...
               PH_init), PH_coarse);

% preliminary spectrum after phasing and baseline correction
prelim_spectrum = finalize_spec(phased_coarse,PH_fine,pks,f);

% test for maximum peak and if negative, apply a correction to the
               phasing
% parameters

[M,I] = max(abs(prelim_spectrum(:,2)));
if prelim_spectrum(I,2) < 0
    final_spectrum = finalize_spec(phased_coarse,PH_fine+180,pks,f);
else
    final_spectrum = prelim_spectrum;
end

% convert the spectrum from x-axis showing frequency to the chemical
               shift
% scale; default values for the reference is the water chemical shift
               4.74
% ppm and the resonance of the Spinsolve with 43.5 Hz

ppm_spectrum=chemical_shift(final_spectrum,f);
ppm_raw=chemical_shift(spectrum_shifted,f);
```

```
% figure
% plot(ppm_raw(:,1),ppm_raw(:,2),ppm_spectrum(:,1),ppm_spectrum(:,2))
% set(gca,'XDir','Reverse')
% xlabel('chemical shift / ppm')
% xlim([-5 15])
% ylabel('signal amplitude')
% legend('unprocessed', 'processed')

ppm_scale=ppm_spectrum(:,1);
[~,idx1]=min(abs(ppm_scale-10));
[~,idx2]=min(abs(ppm_scale+5));
amplitude=ppm_spectrum(idx1:idx2,2);
scale=ppm_spectrum(idx1:idx2,1);

% determine oil concentration in the produced water, input parameters
% need
% to be defined (these are provided by the user as input parameters
% when
% used with LabVIEW
% V_PW = 150; % [mL]
% V_ELUTE = 10; % [mL]
% CONC_REF = 1; % [%]
% RHO_OIL = 0.8183; % [g/mL]

totalOil = calc_total_oil(ppm_spectrum,RHO_OIL,CONC_REF,V_PW,V_ELUTE)
;
```

D.2 Functions

Functions called from the main Matlab script in alphabetical order.

```
function [c_oil_pw] = calc_total_oil(spectrum,rho_oil,c_ref,V_pw,
    V_elute)

rho_ref = 1.4888; %[g/mL] depends on the reference used, CHCl3 here

M_ref = 119.38; % [g/mol] depends on reference used, CHCl3 in this
    case
HI_oil = 9 * rho_oil * (0.15 + 0.2 * (0.9 - rho_oil)^2);
HI_ref = rho_ref / (M_ref * 0.111);
```

```

%integral ranges for reference: 6 to 8.5 ppm
ref_low = 6.25;
ref_up = 8.25;
[~,in_ref_low] = min(abs(spectrum(:,1)-ref_low));
[~,in_ref_up] = min(abs(spectrum(:,1)-ref_up));
A_ref = trapz(spectrum(in_ref_up:in_ref_low,2));
%integral ranges for aliphatic oil: -1 to 3 ppm
oil_low = 0;
oil_up = 2.5;
[~,in_oil_low] = min(abs(spectrum(:,1)-oil_low));
[~,in_oil_up] = min(abs(spectrum(:,1)-oil_up));
A_oil = trapz(spectrum(in_oil_up:in_oil_low,2));

% input parameters
% V_pw = 150 ; % [mL]
% V_elute = 10; % [mL]

% calculate ref volume in sample
V_ref = c_ref / 100 * V_elute; % [mL]

m_oil = (A_oil * HI_ref) / (A_ref * HI_oil) * V_ref * rho_oil * 1000;
      %[mg]

c_oil_pw = m_oil / V_pw * 1000;

end

function [chem_shift_spectrum]=chemical_shift(spectrum_zero,freq,
    varargin)
%   converts the frequency spectrum into a spectrum with chemical
%   shift as
%   x-axis
%   Input arguments:   spectrum = matrix containing frequency in
%                       column
%
%                       one and the complex signal points
%   varargin = optional arguments, if the user
%   does
%
%                       not input the chemical shift of the
%   reference and the resonance,
%   default
%
%                       values are selected;
%   ref = value of the chemical shift
%   reference,

```

Matlab Algorithm for Spinsolve Data Processing

```
%                                should be 4.74 for the Spinsolve (
    H2O)
%                                resonance =resonance frequency of the
%                                spectrometer, 43.5 ppm for the
    Spinsolve
spectrum=[freq,spectrum_zero(:,2)];
numvarargs = length(varargin);
if numvarargs > 2
    error('chem_shift:TooManyInputs','requires at most 2 optional
        inputs');
end

%set defaults for the optional inputs chemical shift reference and
%resonance of the spectrometer
optargs = {4.74 43.5}; % [ppm] and [Hz]; water reference is at 4.74
    ppm,
% chemical shift to base the rest on, occurs at zero frequency
%(shifted spectrum)

% transfer the defaults into a valuesToUse cell array and overwrite
    the
% ones specified in varargin.
optargs(1:numvarargs) = varargin;

% use memorable variable names to access the values in the following
    code
[ref, resonance] = optargs{:};
chem_shift=ref-spectrum(:,1)./resonance;
chem_shift_spectrum=[chem_shift,spectrum(:,2)];

end

function [peaks,baseline_points,noise_ave,spec_basecorrected]=...
    extractBase(spectrum,N_window,smooth_width,k)
% Function for the automatic baseline-correction of a frequency
    domain,
% complex NMR spectrum
% includes:      baseline recognition - threshold that determines if
    point i
%                belongs to the baseline or to a peak
%                baseline modeling - uses fastsmooth to interpolate
    between
%                the points previously identified as baseline points
    sub-
```

```

%           traction of the baseline model from the original
% spectrum
% Input:    raw_spectrum = two column matrix with frequency and
%           complex
%           signal, spectrum to be baseline corrected
%           N_window = width of window with ith-point at center,
%           to
%           calculate if point i belongs to baseline
%           k = factor for multiplication with minimum
%           noise
%           value to determine threshold for baseline
%           recognition
%           smooth_width = number of points to include for smoothing
%           the
%           baseline model
% Output:   peaks = all the data points that are not part of
%           the
%           baseline (peak points)
%           baseline_points = contains all the points recognized as
%           the
%           baseline
%           noise_min = minimum standard deviation = noise value
%           of the
%           spectrum
%           spec_basecorrected = baseline corrected spectrum with max
%           peak
%           at 0 Hz

% spectrum is divided in 64 parts; for each, the standard deviation
% is
% calculated and stored in "noise"; of these values, the minimum is
% chosen
% "noise_min" for further calculations
N=length(spectrum);
noise=[N/128;1];
m=1;
for i=1:N/128:length(spectrum)-64
    noise(m,1)=std(spectrum(i:i+N/128-1,2));
    m=m+1;
end
noise_ave = mean(noise);
noise_min=min(noise);

```

```
% calculation of the difference between the maximum and the minimum
value
% for a window of width N_window centered around each point i of the
% spectrum: a matrix is constructed consisting of the frequency, the
% difference and the original value of each point (indexed i)
diff_y=[N/N_window;4];
m=1;
for i=N_window/2+1:length(spectrum)-N_window/2
    diff_y(m,1)=spectrum(i,1); % frequency of point i
    diff_y(m,2)=max(spectrum((i-N_window/2:i+N_window/2-1),2))...
        -min(spectrum((i-N_window/2:i+N_window/2-1),2));
    %difference between maximum and minimum value
    diff_y(m,3)=spectrum(i,2); % respective complex point
    m=m+1;
end

% determine if point i belongs to the baseline or a peak i; for this,
the
% difference ymax-ymin is compared to k*noise_min and if smaller, i
is a
% baseline point
% all points recognized as baseline points are collected into a
matrix -
% frequency plus complex signal point
%baseline_points=[length(diff_y);2];
m=1;
s=1;
for i=1:length(diff_y)
    if diff_y(i,2)< k*noise_min
        baseline_points(m,1)=diff_y(i,1);
        baseline_points(m,2)=diff_y(i,3);
        m=m+1;
    else
        peaks(s,1)=diff_y(i,1);
        peaks(s,2)=diff_y(i,3);
        s=s+1;
    end
end
end
```

```
% model the baseline by smoothing (averaging) with a rectangular
    function,
% interpolation is then used to determine the points between the
% baseline points to get to the number of complex points of the
    original
% spectrum
% Result is a 2-column matrix with frequency data and the baseline
    model
% points
S=fastsmooth(baseline_points(:,2),smooth_width,3,0);
S_inter=interp1(baseline_points(:,1),S,spectrum(:,1));
smooth_spectrum=[spectrum(:,1),S_inter];

% subtraction of the modeled baseline from the original spectrum to
    get a
% spectrum with corrected (flat) baseline
% here only the complex point are determined

Y_basecorrected=[N;1];
n=1;
for i=1:length(spectrum)
    Y_basecorrected(n)=spectrum(i,2)-smooth_spectrum(i,2);
    n=n+1;
end

% final step to combine the frequency data and the baseline corrected
% complex point into one matrix
% output of the function
spec_basecorrected=[spectrum(:,1),Y_basecorrected];
end

function [peak_data]=extractPeaks(base_corrected_spectrum, noise_SD,
    freq)
% Function to extract peak data (indices, frequency and amplitude)
    from the
% spectra

% Input parameters:
%   Y_real          = vector containing the real Y data of the
        spectrum
%   noise_SD        = noise value of the spectrum
%   freq            = vector with the frequency data points
%
```


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```
% Output parameters:
% peak_data      = matrix with three columns and rows according to
%                 the
%                 number of peaks detected, column 1 = peak indices,
%                 where to find the peaks in the complete data set,
%                 column 2 = peak frequency values, column 3 =
%                 amplitude
%                 of the respective peak

Y_real=real(base_corrected_spectrum(:,2));
% findpeaks extracts the peaks (maximum amplitude) from the spectrum
% according to the noise threshold and peak prominence selected
pks_ampl = findpeaks(Y_real,'MinPeakHeight',20*noise_SD,...
                    'MinPeakProminence',10*noise_SD);
m=1;
pks_index=length(pks_ampl); % initialize vector
pks_freq=length(pks_ampl);
% for all detected peaks extract the data point index and frequency
for i = 1 : length(pks_ampl)
    pks_index(m) = find(Y_real == pks_ampl(i));
    pks_freq(m) = freq(pks_index(m));
    m=m+1;
end

% join all data into one matrix
peak_data = [pks_index.', pks_freq.', pks_ampl];
end

function peakInfo = extractTails(frequency, df, peaks_compl,
                                peaks_max, PN)
% Function to extract the position of the tails to each detected peak
% from
% the peak matrix and puts it into a two-column matrix

% Input parameters:
% frequency      = frequency data points
% df             = frequency increment between two points
% peaks_compl    = matrix that contains frequency data and real points
%                 of
%                 only the detected peaks (not the baseline points)
% peaks_max      = matrix with data point no., freq value and
%                 amplitude
```

```

%           of the detected peaks
%   PN           = number of peaks that were detected

%   Output parameters:
%   peakInfo     = matrix with two columns and PN - x rows, where x is
%                 the
%                 number of shoulder or multiplets, first column
%                 contains
%                 the tail start index and the second column the tail
%                 end
%                 index

freq=peaks_compl(:,1);
maxfreq=peaks_max(:,2);
peakInfo=[PN, 2];
l=1;
for i = 1:size(peaks_max,1)
    k = find(freq == maxfreq(i));
    diff_freq = df;
    while diff_freq <= df+0.1
        k = k-1;
        if k == 1
            break
        end
        diff_freq = freq(k)-freq(k-1);
    end
    if l == 1 || find(frequency == freq(k)) ~= peakInfo(l-1,1)
        peakInfo(l,1)=find(frequency == freq(k));
        l=l+1;
    end
end

end

m=1;
for i = 1:size(peaks_max,1)
    k = find(freq == maxfreq(i));
    diff_freq = df;
    while diff_freq <= df+0.1
        k = k+1;
        diff_freq = freq(k+1)-freq(k);
    end
    if m == 1 || find(frequency == freq(k)) ~= peakInfo(m-1,2)

```

Matlab Algorithm for Spinsolve Data Processing

```
        peakInfo(m,2)=find(frequency == freq(k));
        m=m+1;
    end

end

peakInfo(:,1) = unique(peakInfo(:,1));
peakInfo(:,2) = unique(peakInfo(:,2));

end

function SmoothY=fastsmooth(Y,w,type,ends)
% fastsmooth(Y,w,type,ends) smooths vector Y with smooth
% of width w. Version 2.0, May 2008.
% The argument "type" determines the smooth type:
%   If type=1, rectangular (sliding-average or boxcar)
%   If type=2, triangular (2 passes of sliding-average)
%   If type=3, pseudo-Gaussian (3 passes of sliding-average)
% The argument "ends" controls how the "ends" of the signal
% (the first w/2 points and the last w/2 points) are handled.
%   If ends=0, the ends are zero. (In this mode the elapsed
%   time is independent of the smooth width). The fastest.
%   If ends=1, the ends are smoothed with progressively
%   smaller smooths the closer to the end. (In this mode the
%   elapsed time increases with increasing smooth widths).
% fastsmooth(Y,w,type) smooths with ends=0.
% fastsmooth(Y,w) smooths with type=1 and ends=0.
% Example:
% fastsmooth([1 1 1 10 10 10 1 1 1 1],3)= [0 1 4 7 10 7 4 1 1 0]
% fastsmooth([1 1 1 10 10 10 1 1 1 1],3,1,1)= [1 1 4 7 10 7 4 1 1 1]
% T. C. O'Haver, May, 2008.
if nargin==2, ends=0; type=1; end
if nargin==3, ends=0; end
switch type
    case 1
        SmoothY=sa(Y,w,ends);
    case 2
        SmoothY=sa(sa(Y,w,ends),w,ends);
    case 3
        SmoothY=sa(sa(sa(Y,w,ends),w,ends),w,ends);
end

function SmoothY=sa(Y,smoothwidth,ends)
```

```

w=round(smoothwidth);
SumPoints=sum(Y(1:w));
s=zeros(size(Y));
halfw=round(w/2);
L=length(Y);
for k=1:L-w,
    s(k+halfw-1)=SumPoints;
    SumPoints=SumPoints-Y(k);
    SumPoints=SumPoints+Y(k+w);
end
s(k+halfw)=sum(Y(L-w+1:L));
SmoothY=s./w;
% Taper the ends of the signal if ends=1.
if ends==1,
    startpoint=(smoothwidth + 1)/2;
    SmoothY(1)=(Y(1)+Y(2))./2;
    for k=2:startpoint,
        SmoothY(k)=mean(Y(1:(2*k-1)));
        SmoothY(L-k+1)=mean(Y(L-2*k+2:L));
    end
    SmoothY(L)=(Y(L)+Y(L-1))./2;
end

function [Y_real, Yshift, freq_shift_max, spectrum_shifted] =...
    fid_transform(fid, N_data, freq)
% Fourier transformation of the time domain data received from the
% Spinsolve

% Input          fid      array containing all data received from
%               the
%               Spinsolve, time and complex data points
%               in
%               sequence
%               N_data    number of data points in the spectrum
%               freq      vector containing the frequency points

% Output          Y_real: vector with real data points of the
%               spectrum
%               freq_spectrum: matrix containing the frequency
%               and the
%               shifted complex spectrum
%               spectrum_shifted: largest peak at 0 Hz (necessary
%               for

```

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```
%                                     phasing algorithm to apply
    correct
%                                     p0 correction)

Y=fft(fid(:,2))/N_data; % fourier transformation of the complex time
    domain
% signal which is contained in the second column of the fid_matrix,
% dividing by N is for normalization
Yshift=fftshift(Y); %shift zero-frequency component to the center

[ampl, index_freq] = max(Yshift);
freq_max=freq(index_freq);
freq_shift_max=freq-freq_max;
spectrum_shifted=[freq_shift_max,Yshift];

Y_real=real(spectrum_shifted(:,2)); %real part of the spectrum

end

function [final_spectrum] = finalize_spec(spectrum,PH,peak_info,freq)
% Function to calculate the phased spectrum

prelim_spectrum=phase(spectrum,PH);
[row,col]=find(~peak_info);
x=peak_info(row,1);
ampl_real=real(prelim_spectrum(:,2));
if ampl_real(x) < 0
    PH_correct = PH + 180;
else
    PH_correct = PH;
end

prelim2_spectrum=phase(spectrum,PH_correct);
final_spectrum=[freq,prelim2_spectrum(:,2)];

end

function PF = fine_tune(spectrum,tails, PH)
%UNTITLED Summary of this function goes here
% Detailed explanation goes here
% , peak_data
```

```
phased_spec=phase(spectrum,PH);

%phased_spec = baselinecorrection(phased_spec,64,4.5,32);

m=1;

peak_height = [size(tails(1),1),1];

if size(tails,1) == 1
    peak_height = max(phased_spec(tails(1):tails(2),2));
else
    for i = 1 : size(tails,1)
        peak_height(m) = max(phased_spec(tails(i,1):tails(i,2),2));
        m = m+1;
    end
end

TempR=[length(spectrum),1];
n=1;

for i = 1 : length(peak_height)
    for j = tails(i,1) : tails(i,2)
```

```
        else
            TempR(n) = phased_spec(j,2);
            n = n + 1;
        end
    end
end

penalty=(TempR(i)-abs(TempR(i)))^2;

PF = sum(penalty);

end

function [x,fval,exitflag,output] = fminsearch2(funfcn,x,options,
    varargin)
% Multidimensional unconstrained nonlinear minimization (Nelder-Mead)
%
%   X = FMINSEARCH(FUN,X0) starts at X0 and attempts to find a local
%   minimizer X of the function FUN.  FUN is a function handle. FUN
%   accepts input X and returns a scalar function value F evaluated
%   at X.
%
%   X0 can be a scalar, vector or matrix.
%
%   X = FMINSEARCH(FUN,X0,OPTIONS) minimizes with the default
%   optimization
%   parameters replaced by values in the structure OPTIONS, created
%   with the OPTIMSET function.  See OPTIMSET for details. FMINSEARCH
%   uses
%   these options: Display, TolX, TolFun, MaxFunEvals, MaxIter,
%   FunValCheck,
%   PlotFcns, and OutputFcn.
%
%   X = FMINSEARCH(PROBLEM) finds the minimum for PROBLEM. PROBLEM is
%   a
%   structure with the function FUN in PROBLEM.objective, the start
%   point
%   in PROBLEM.x0, the options structure in PROBLEM.options, and
%   solver
%   name 'fminsearch' in PROBLEM.solver. The PROBLEM structure must
%   have
%   all the fields.
%
%   [X,FVAL]= FMINSEARCH(...) returns the value of the objective
%   function,
```

```

%   described in FUN, at X.
%
%   [X,FVAL,EXITFLAG] = FMINSEARCH(...) returns an EXITFLAG that
describes
%   the exit condition of FMINSEARCH. Possible values of EXITFLAG and
the
%   corresponding exit conditions are
%
%   1   Maximum coordinate difference between current best point and
other
%       points in simplex is less than or equal to TolX, and
corresponding
%       difference in function values is less than or equal to TolFun
.
%   0   Maximum number of function evaluations or iterations reached.
%   -1  Algorithm terminated by the output function.
%
%   [X,FVAL,EXITFLAG,OUTPUT] = FMINSEARCH(...) returns a structure
%   OUTPUT with the number of iterations taken in OUTPUT.iterations,
the
%   number of function evaluations in OUTPUT.funcCount, the algorithm
name
%   in OUTPUT.algorithm, and the exit message in OUTPUT.message.
%
%   Examples
%       FUN can be specified using @:
%       X = fminsearch(@sin,3)
%       finds a minimum of the SIN function near 3.
%       In this case, SIN is a function that returns a scalar function
value
%       SIN evaluated at X.
%
%       FUN can be an anonymous function:
%       X = fminsearch(@(x) norm(x),[1;2;3])
%       returns a point near the minimizer [0;0;0].
%
%       FUN can be a parameterized function. Use an anonymous function
to
%       capture the problem-dependent parameters:
%       f = @(x,c) x(1).^2+c.*x(2).^2; % The parameterized function
.
%       c = 1.5; % The parameter.
%       X = fminsearch(@(x) f(x,c),[0.3;1])

```


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```
%
%   FMINSEARCH uses the Nelder-Mead simplex (direct search) method.
%
%   See also OPTIMSET, FMINBND, FUNCTION_HANDLE.

%   Reference: Jeffrey C. Lagarias, James A. Reeds, Margaret H.
%   Wright,
%   Paul E. Wright, "Convergence Properties of the Nelder-Mead
%   Simplex
%   Method in Low Dimensions", SIAM Journal of Optimization, 9(1):
%   p.112-147, 1998.

%   Copyright 1984-2012 The MathWorks, Inc.

defaultopt =struct('Display','notify','MaxIter','200*
    numberOfVariables',...
    'MaxFunEvals','200*numberOfVariables','TolX',1e-4,'TolFun',1e-4,
    ...
    'FunValCheck','off','OutputFcn',[],'PlotFcns',[]);

% If just 'defaults' passed in, return the default options in X
if nargin==1 && narginout <= 1 && isequal(funfcn,'defaults')
    x = defaultopt;
    return
end

if nargin<3, options = []; end

% Detect problem structure input
if nargin == 1
    if isa(funfcn,'struct')
        [funfcn,x,options] = separateOptimStruct(funfcn);
    else % Single input and non-structure
        error(message('MATLAB:fminsearch:InputArg'));
    end
end

if nargin == 0
    error(message('MATLAB:fminsearch:NotEnoughInputs'));
end
```

```
% Check for non-double inputs
if ~isa(x,'double')
    error(message('MATLAB:fminsearch:NonDoubleInput'))
end

n = numel(x);
numberOfVariables = n;

prnttype = optimget(options,'Display',defaultopt,'fast');
tolx = optimget(options,'TolX',defaultopt,'fast');
tolf = optimget(options,'TolFun',defaultopt,'fast');
maxfun = optimget(options,'MaxFunEvals',defaultopt,'fast');
maxiter = optimget(options,'MaxIter',defaultopt,'fast');
funValCheck = strcmp(optimget(options,'FunValCheck',defaultopt,'fast'
    ),...
        'on');

% In case the defaults were gathered from calling: optimset('
    fminsearch'):
if ischar(maxfun)
    if isequal(lower(maxfun),'200*numberOfvariables')
        maxfun = 200*numberOfVariables;
    else
        error(message('MATLAB:fminsearch:OptMaxFunEvalsNotInteger'))
    end
end
if ischar(maxiter)
    if isequal(lower(maxiter),'200*numberOfvariables')
        maxiter = 200*numberOfVariables;
    else
        error(message('MATLAB:fminsearch:OptMaxIterNotInteger'))
    end
end

switch prnttype
    case {'notify','notify-detailed'}
        prnt = 1;
    case {'none','off'}
        prnt = 0;
    case {'iter','iter-detailed'}
        prnt = 3;
    case {'final','final-detailed'}
        prnt = 2;
```

```
        case 'simplex'
            prnt = 4;
        otherwise
            prnt = 1;
    end
% Handle the output
outputfcn = optimget(options,'OutputFcn',defaultopt,'fast');
if isempty(outputfcn)
    haveoutputfcn = false;
else
    haveoutputfcn = true;
    xOutputfcn = x; % Last x passed to outputfcn; has the input x's
                    shape
    % Parse OutputFcn which is needed to support cell array syntax
    for
    % OutputFcn.
    outputfcn = createCellArrayOfFunctions(outputfcn,'OutputFcn');
end

% Handle the plot
plotfcns = optimget(options,'PlotFcns',defaultopt,'fast');
if isempty(plotfcns)
    haveplotfcn = false;
else
    haveplotfcn = true;
    xOutputfcn = x; % Last x passed to plotfcns; has the input x's
                    shape
    % Parse PlotFcns which is needed to support cell array syntax for
    % PlotFcns.
    plotfcns = createCellArrayOfFunctions(plotfcns,'PlotFcns');
end

header = ' Iteration      Func-count      min f(x)          Procedure';

% Convert to function handle as needed.
funfcn = fcnchk(funfcn,length(varargin));
% Add a wrapper function to check for Inf/NaN/complex values
if funValCheck
    % Add a wrapper function, CHECKFUN, to check for NaN/complex
    values
    % without having to change the calls that look like this:
    % f = funfcn(x,varargin{:});
    % x is the first argument to CHECKFUN, then the user's function,
```

```

    % then the elements of varargin. To accomplish this we need to
    % add the
    % user's function to the beginning of varargin, and change funfcn
    % to be
    % CHECKFUN.
    varargin = {funfcn, varargin{:}};
    funfcn = @checkfun;
end

n = numel(x);

% Initialize parameters
rho = 1; chi = 2; psi = 0.5; sigma = 0.5;
onesn = ones(1,n);
two2np1 = 2:n+1;
one2n = 1:n;

% Set up a simplex near the initial guess.
xin = x(:); % Force xin to be a column vector
v = zeros(n,n+1); fv = zeros(1,n+1);
v(:,1) = xin; % Place input guess in the simplex!
% (credit L.Pfeffer at Stanford)
x(:) = xin; % Change x to the form expected by funfcn
fv(:,1) = funfcn(x,varargin{:});
func_evals = 1;
itercount = 0;
how = '';
% Initial simplex setup continues later

% Initialize the output and plot functions.
if haveoutputfcn || haveplotfcn
    [xOutputfcn, optimValues, stop] = callOutputAndPlotFcns(outputfcn
        , ...
        plotfcns,v(:,1),xOutputfcn,'init',itercount, ...
        func_evals, how, fv(:,1),varargin{:});
    if stop
        [x,fval,exitflag,output] = cleanUpInterrupt(xOutputfcn,
            optimValues);
        if prnt > 0
            disp(output.message)
        end
        return;
    end
end
end

```

Matlab Algorithm for Spinsolve Data Processing

```
end

% Print out initial f(x) as 0th iteration
if prnt == 3
    disp(' ')
    disp(header)
    fprintf(' %5.0f          %5.0f          %12.6g          %s\n', ...
        itercount, func_evals, fv(1), how);
elseif prnt == 4
    clc
    formatsave.format = get(0,'format');
    formatsave.formatspacing = get(0,'formatspacing');
    % reset format when done
    oc1 = onCleanup(@()set(0,'format',formatsave.format));
    oc2 = onCleanup(@()set(0,'formatspacing',formatsave.formatspacing
        ));
    format compact
    format short e
    disp(' ')
    disp(how)
    v
    fv
    func_evals
end
% OutputFcn and PlotFcns call
if haveoutputfcn || haveplotfcn
    [xOutputfcn, optimValues, stop] = callOutputAndPlotFcns(outputfcn
        , ...
        plotfcns,v(:,1),xOutputfcn,'iter',itercount, ...
        func_evals, how, fv(:,1),varargin{:});
    if stop % Stop per user request.
        [x,fval,exitflag,output] =cleanUpInterrupt(xOutputfcn,
            optimValues);
        if prnt > 0
            disp(output.message)
        end
        return;
    end
end
end

% Continue setting up the initial simplex.
% Following improvement suggested by L.Pfeffer at Stanford
usual_delta = 0.05; % 5 percent deltas for non-zero terms
```

```

zero_term_delta = 1;          % Even smaller delta for zero elements of x
for j = 1:n
    y = xin;
    if y(j) ~= 0
        y(j) = (1 + usual_delta)*y(j);
    else
        y(j) = zero_term_delta;
    end
    v(:,j+1) = y;
    x(:) = y; f = funfcn(x,varargin{:});
    fv(1,j+1) = f;
end

% sort so v(1,:) has the lowest function value
[fv,j] = sort(fv);
v = v(:,j);

how = 'initial simplex';
itercount = itercount + 1;
func_evals = n+1;
if prnt == 3
    fprintf(' %5.0f          %5.0f          %12.6g          %s\n', ...
            itercount, func_evals, fv(1), how)
elseif prnt == 4
    disp(' ')
    disp(how)
    v
    fv
    func_evals
end
% OutputFcn and PlotFcns call
if haveoutputfcn || haveplotfcn
    [xOutputfcn, optimValues, stop] = callOutputAndPlotFcns(outputfcn
        , ...
        plotfcns,v(:,1),xOutputfcn,'iter',itercount, ...
        func_evals, how, fv(:,1),varargin{:});
    if stop % Stop per user request.
        [x,fval,exitflag,output] =cleanUpInterrupt(xOutputfcn,
            optimValues);
        if prnt > 0
            disp(output.message)
        end
    end
    return;

```

```

    end
end
exitflag = 1;

% Main algorithm: iterate until
% (a) the maximum coordinate difference between the current best
    point and
% the other points in the simplex is less than or equal to TolX.
% Specifically, until max(||v2-v1||,||v2-v1||,...,||v(n+1)-v1||) <=
    TolX,
% where ||.|| is the infinity-norm, and v1 holds the
% vertex with the current lowest value; AND
% (b) the corresponding difference in function values is less than or
    equal
% to TolFun. (Cannot use OR instead of AND.)
% The iteration stops if the maximum number of iterations or function
% evaluations are exceeded
while func_evals < maxfun && itercount < maxiter
    if max(abs(fv(1)-fv(two2np1))) <= max(tolf,10*eps(fv(1))) && ...
        max(max(abs(v(:,two2np1)-v(:,onesn)))) <= max(tolx,10*eps(max(v
            (:,1))))
        break
    end

    % Compute the reflection point

    % xbar = average of the n (NOT n+1) best points
    xbar = sum(v(:,one2n), 2)/n;
    xr = (1 + rho)*xbar - rho*v(:,end);
    x(:) = xr; fxr = funfcn(x,varargin{:});
    func_evals = func_evals+1;

    if fxr < fv(:,1)
        % Calculate the expansion point
        xe = (1 + rho*chi)*xbar - rho*chi*v(:,end);
        x(:) = xe; fxe = funfcn(x,varargin{:});
        func_evals = func_evals+1;
        if fxe < fxr
            v(:,end) = xe;
            fv(:,end) = fxe;
            how = 'expand';
        else
            v(:,end) = xr;

```

```

        fv(:,end) = fxr;
        how = 'reflect';
    end
else % fv(:,1) <= fxr
    if fxr < fv(:,n)
        v(:,end) = xr;
        fv(:,end) = fxr;
        how = 'reflect';
    else % fxr >= fv(:,n)
        % Perform contraction
        if fxr < fv(:,end)
            % Perform an outside contraction
            xc = (1 + psi*rho)*xbar - psi*rho*v(:,end);
            x(:) = xc; fxc = funfcn(x,varargin{:});
            func_evals = func_evals+1;

            if fxc <= fxr
                v(:,end) = xc;
                fv(:,end) = fxc;
                how = 'contract outside';
            else
                % perform a shrink
                how = 'shrink';
            end
        else
            % Perform an inside contraction
            xcc = (1-psi)*xbar + psi*v(:,end);
            x(:) = xcc; fxcc = funfcn(x,varargin{:});
            func_evals = func_evals+1;

            if fxcc < fv(:,end)
                v(:,end) = xcc;
                fv(:,end) = fxcc;
                how = 'contract inside';
            else
                % perform a shrink
                how = 'shrink';
            end
        end
    end
end
if strcmp(how, 'shrink')
    for j=two2np1
        v(:,j)=v(:,1)+sigma*(v(:,j) - v(:,1));
        x(:) = v(:,j); fv(:,j) = funfcn(x,varargin{:});
    end
end

```



```

        end
        func_evals = func_evals + n;
    end
end
end
[fv,j] = sort(fv);
v = v(:,j);
itercount = itercount + 1;
if prnt == 3
    fprintf(' %5.0f      %5.0f      %12.6g      %s\n', ...
            itercount, func_evals, fv(1), how)
elseif prnt == 4
    disp(' ')
    disp(how)
    v
    fv
    func_evals
end
% OutputFcn and PlotFcns call
if haveoutputfcn || haveplotfcn
    [xOutputfcn, optimValues, stop] = callOutputAndPlotFcns(...
        outputfcn,plotfcns,v(:,1),xOutputfcn,'iter',itercount,
        ...
        func_evals, how, fv(:,1),varargin{:});
    if stop % Stop per user request.
        [x,fval,exitflag,output] = cleanUpInterrupt(xOutputfcn
            ,...
            optimValues);
        if prnt > 0
            disp(output.message)
        end
        return;
    end
end
end % while

x(:) = v(:,1);
fval = fv(:,1);

output.iterations = itercount;
output.funcCount = func_evals;
output.algorithm = 'Nelder-Mead simplex direct search';

```

```
% OutputFcn and PlotFcns call
if haveoutputfcn || haveplotfcn
    callOutputAndPlotFcns(outputfcn,plotfcns,x,xOutputfcn,'done',...
        itercount, func_evals, how, fval, varargin{:});
end

if func_evals >= maxfun
    msg = getString(message('MATLAB:fminsearch:
        ExitingMaxFunctionEvals',...
        sprintf('%f',fval)));
    if prnt > 0
        disp(' ')
        disp(msg)
    end
    exitflag = 0;
elseif itercount >= maxiter
    msg = getString(message('MATLAB:fminsearch:ExitingMaxIterations'
        ,...
        sprintf('%f',fval)));
    if prnt > 0
        disp(' ')
        disp(msg)
    end
    exitflag = 0;
else
    msg = ...
        getString(message(...
            'MATLAB:fminsearch:OptimizationTerminatedXSatisfiesCriteria',
            ...
            sprintf('%e',tolx), sprintf('%e',tolf)));
    if prnt > 1
        disp(' ')
        disp(msg)
    end
    exitflag = 1;
end

output.message = msg;

%
-----

function [xOutputfcn, optimValues, stop] = callOutputAndPlotFcns(...
```

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```
        outputfcn,plotfcns,x,xOutputfcn,state,iter,...
        numf,how,f,varargin)
% CALLOUTPUTANDPLOTFCNS assigns values to the struct OptimValues and
    then calls the
% outputfcn/plotfcns.
%
% state - can have the values 'init','iter', or 'done'.

% For the 'done' state we do not check the value of 'stop' because
    the
% optimization is already done.
optimValues.iteration = iter;
optimValues.funccount = numf;
optimValues.fval = f;
optimValues.procedure = how;

xOutputfcn(:) = x; % Set x to have user expected size
stop = false;
% Call output functions
if ~isempty(outputfcn)
    switch state
        case {'iter','init'}
            stop = callAllOptimOutputFcns(outputfcn,xOutputfcn,...
                optimValues,state,varargin{:}) || stop;
        case 'done'
            callAllOptimOutputFcns(outputfcn,xOutputfcn,...
                optimValues,state,varargin{:});
        otherwise
            error(message('MATLAB:fminsearch:InvalidState'))
    end
end
% Call plot functions
if ~isempty(plotfcns)
    switch state
        case {'iter','init'}
            stop = callAllOptimPlotFcns(plotfcns,xOutputfcn,...
                optimValues,state,varargin{:}) || stop;
        case 'done'
            callAllOptimPlotFcns(plotfcns,xOutputfcn,...
                optimValues,state,varargin{:});
        otherwise
            error(message('MATLAB:fminsearch:InvalidState'))
    end
end
```

```
end

%
-----

function [x,FVAL,EXITFLAG,OUTPUT] =cleanUpInterrupt(xOutputfcn,
    optimValues)
% CLEANUPINTERRUPT updates or sets all the output arguments of
    FMINBND
% when the optimization is interrupted.

% Call plot function driver to finalize the plot function figure
    window. If
% no plot functions have been specified or the plot function figure
    no
% longer exists, this call just returns.
callAllOptimPlotFcns('cleanuponstopsignal');

x = xOutputfcn;
FVAL = optimValues.fval;
EXITFLAG = -1;
OUTPUT.iterations = optimValues.iteration;
OUTPUT.funcCount = optimValues.funccount;
OUTPUT.algorithm = 'Nelder-Mead simplex direct search';
OUTPUT.message = getString(message(...
    'MATLAB:fminsearch:OptimizationTerminatedPrematurelyByUser'));

%
-----

function f = checkfun(x,userfcn,varargin)
% CHECKFUN checks for complex or NaN results from userfcn.

f = userfcn(x,varargin{:});
% Note: we do not check for Inf as FMINSEARCH handles it naturally.
if isnan(f)
    error(message('MATLAB:fminsearch:checkfun:NaNFval',...
        localChar(userfcn)));
elseif ~isreal(f)
    error(message('MATLAB:fminsearch:checkfun:ComplexFval', ...
        localChar( userfcn )));
end
```

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```
%
-----

function strfcn = localChar(fcn)
% Convert the fcn to a string for printing

if ischar(fcn)
    strfcn = fcn;
elseif isa(fcn,'inline')
    strfcn = char(fcn);
elseif isa(fcn,'function_handle')
    strfcn = func2str(fcn);
else
    try
        strfcn = char(fcn);
    catch
        strfcn = getString(message('MATLAB:fminsearch:
            NameNotPrintable')));
    end
end

function [OF] =objective_function(M, spec, PH, tails)
%Objective function that calculates the height differences between
the
%starts and ends of the detected peaks in the spectrum

%   Input parameters:
%
%   M           = number of chosen points for the tail ends of the
peaks
%               (start and end must be the same)
%   spec        = spectral data consisting of frequency data and
complex
%               points
%   PH          = initial phase guess, usually [0,0]
%   peakInfo    = matrix containing the start and end data point
numbers of
%               the peaks, row numbers are equal to PN;

%   Output paramater:
%   OF =   objective function that is then subject to fminsearch,
find
%               minimum at PH
```

```

PN = size(tails,1);
m=1;
p=1;
abs_diff=[PN;1];
R_start=[M;1];
R_end=[M;1];

if PN == 1
    for k = 0 : M
        R_start(m) = phase2(spec,PH,tails(1)-k);
        R_end(m) = phase2(spec,PH,tails(2)+k);
        m=m+1;
    end
    abs_diff = abs (sum(R_start) - sum(R_end));
else
    for i=1:PN
        for k = 0 : M
            R_start(m) = phase2(spec,PH,tails(i,1)-k);
            R_end(m) = phase2(spec,PH,tails(i,2)+k);
            m=m+1;
        end
        abs_diff(p) = abs (sum(R_start) - sum(R_end));
        p=p+1;
    end
end
OF = sum(abs_diff);
end

function spec_phased = phase(spectrum,PH)
% Function to phase the complx spectrum with the passed phase angles
% p0
% and p1

% Input parameters
% freq      = vector with the frequency points
% spec      = vector containing the complex data points of the
%             spectrum
% PH        = phase angles p0 and p1 in a row vector

% Output parameter
% spec_phased = matrix with two column containing the frequency
%             data
%             points along with the phased real points of the
%             spectrum

```

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```
% convert the phase angles from degrees to radians
freq=spectrum(:,1);
ampl=spectrum(:,2).';
PH = PH.*pi./180;

% apply phasing
```

```

start_t=find(data1d_array==0,1); % determines where the actual data
    begins;
% returnsthe index of the row where a zero appears, indicating the
    first
% time point
N_data=(length(data1d_array)-(start_t-1))/3;
% time data starting at zero until acquisition time, N points in
    total
time=data1d_array(start_t:N_data+start_t-1);
%initialize matrix for real component (speeds up the execution of the
    code)
real_part=[N_data;1];
% initialize matrix for imaginary component
imag_part=[N_data;1];
% set index counter to 1
k=1;
for i=N_data+start_t:2:length(data1d_array)
    % separates the real parts and puts them in a matrix
        real_part(k,1)=data1d_array(i);
    % separates the imaginary parts and puts them in a matrix,
    % every second value is the imaginary part
        imag_part(k,1)=data1d_array(i+1);
    % increases the counter by one each time going through the loop
        k=k+1;
end
% time data with the signal - real and imaginary parts are combined
    in a
% complex number - into one matrix, first column is time, second is
    signal
time_domain_spectrum=[time(:), complex(real_part(:), imag_part(:))];
% time increment between points, [s]
delta_t=time_domain_spectrum(2,1)-time_domain_spectrum(1,1);

Nyq=1/(2*delta_t);
%frequency increment between points [Hz]
delta_f=1/(N_data*delta_t);
% frequency vector that stretches from -Nyq to +Nyq with increments
    of df
freq=(-Nyq:delta_f:Nyq-delta_f)';
end

```