Determination of surfactants from foam-formed products

Master's Thesis

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ABSTRACT

In this Master's thesis, determination of surfactant residues from solid foam-formed samples was studied. The residues of an anionic surfactant, sodium dodecyl sulphate (SDS), and a non-ionic surfactant Tween 20 (polyoxyethylenesorbitan monolaurate), were determined from foam-formed hand sheets. The measured surfactant residues were compared with the theoretical values calculated from the water content of the sample before drying phase and the surfactant dosage. In addition to analysis of surfactant residues, determination of 4-dodecylbenzenesulphonic acid (4-DBSA, anionic surfactant) in water solution by UV spectrophotometry was studied. The literature part considers the chemistry of surfactants and introduces the relatively new concept of papermaking, foam forming. The main focus in the literature part is in the analysis methods of surfactants. Sample pre-treatment methods and the use of spectrophotometry, chromatography and atomic spectroscopy in the determination of surfactants are discussed. In addition, the chemical legislation, toxicological concerns of surfactants and the regulations concerning paper and board in food contact materials are discussed.

To determine surfactant residues, two different determination methods were used for both surfactants. SDS residues were determined by spectrophotometry and by inductively coupled plasma optical emission spectrometry (ICP-OES). Tween 20 residues were determined by spectrophotometry and by high-performance liquid chromatography equipped with a diode array detector (HPLC-DAD). Ultrasound-assisted nitric acid digestion was used as a sample preparation method for the ICP-OES analysis. Before the chromatographic determination, Tween 20 was extracted from the sample by methanol in Soxhlet extraction. In the spectrophotometric determination, SDS and Tween 20 were extracted by water.

The results showed that surfactant residues increased as the surfactant dosage increased and when the dry matter content of the sample (before the last drying stage) decreased. ICP-OES and spectrophotometric methods gave very similar results for SDS residues. The results indicated that SDS was effectively extracted from the fibre network by water. The amount of SDS residues was affected by water hardness, the temperature of the water-fibre suspension and the addition of a non-ionic surfactant or cationic starch. When the water hardness was °dH = 5, the measured SDS residues were clearly higher than the theoretical values. This is due to the formation of insoluble calcium dodecyl sulphate $Ca(DS)_2$ that remains in the fibre network. The amount of SDS residues decreased when water hardness decreased, temperature was raised

or a non-ionic surfactant (Tween 20) was added. The addition of cationic starch resulted in the increase of SDS residues.

Tween 20 could be determined by both HPLC-DAD and spectrophotometry. HPLC-DAD gave higher results compared to the spectrophotometric determination, because Tween 20 was not fully extracted by water. When water, ethanol and acetone were compared as extraction solvents in Soxhlet extraction, the results showed clearly that more Tween 20 was extracted by ethanol and acetone than water. The amount of Tween 20 residues was not observed to be higher than theoretically estimated.

TIIVISTELMÄ

Tässä Pro gradu -tutkielmassa tutkittiin surfaktanttien (eli pinta-aktiivisten aineiden) jäämiä kiinteistä vaahtorainatuista näytteistä. Työn päätavoitteena oli kehittää sopivat näytteenkäsittely- ja määritysmenetelmät surfaktanttijäämien määrittämiseksi. Työssä määritettiin yhden anionisen surfaktantin, natrium dodekyylisulfaatin (SDS), ja yhden nonionisen surfaktantin, Tween 20:n (polyoksietyleenisorbitaanimonolauraatti), jäämiä vaahtorainatuista käsiarkeista. Mitattuja surfaktanttijäämiä verrattiin teoreettisiin arvoihin, jotka laskettiin näytteen kuiva-ainepitoisuudesta ennen kuivausvaihetta ja surfaktantin annoksesta. Surfaktanttijäämien analysoinnin lisäksi tutkittiin 4-dodekyylibentseenisulphonihapon (4-DBSA, anioninen surfaktantti) määritystä vesiliuoksesta UV-spektrofotometrillä. Kirjallinen osa käsittelee surfaktanttien kemiaa ja esittelee suhteellisen uuden paperinvalmistusmenetelmän, vaahtorainauksen. Päähuomio on kohdennettu surfaktanttien analyysimenetelmiin. Näytteenkäsittelymenetelmät ja spektrofotometrian, kromatografian sekä atomispektroskopian käyttö surfaktanttien määrityksessä on käsitelty. Lisäksi käydään läpi kemikaalilainsäädäntöä, surfaktantteihin liittyviä toksikologisia huolenaiheita sekä ruokapakkauksissa käytettävää paperia ja kartonkia koskevia säädöksiä.

Surfaktanttijäämien määrittämiseksi käytettiin kahta eri määritysmenetelmää kummallekin surfaktantille. SDS-jäämät määritettiin spektrofotometrillä ja induktiivisesti kytketyllä plasma-optisella emissiospektrometrillä (ICP-OES). Tween 20 -jäämät määritettiin spektrofotometrillä sekä korkean erotuskyvyn nestekromatografilla, jossa oli diodirivi-detektori. ICP-OES -analyysissä näytteenkäsittelymenetelmänä käytettiin ultraääniavustettua typpihappohajotusta. Ennen kromatografista määritystä, Tween 20 uutettiin näytteestä metanolilla käyttäen Soxhlet-uuttoa. Spektrofotometrisessa määrityksessä SDS ja Tween 20 uutettiin veteen.

Tulokset osoittivat, että surfaktanttijäämät kasvoivat, kun surfaktantin annos kasvoi ja kun näytteen kuiva-ainepitoisuus (ennen viimeistä kuivausvaihetta) laski. ICP-OES-laitteella ja spektrofotometrillä saadut tulokset SDS-jäämille olivat hyvin samanlaisia. Tulokset osoittivat, että SDS uuttui kuituverkostosta vedellä tehokkaasti. SDS-jäämien määrään vaikutti näytteen valmistuksessa käytetyn veden kovuus, vesi-kuitu -suspension lämpötila ja nonionisen surfaktantin tai tärkkelyksen lisäys. Kun veden kovuus oli °dH = 5, mitatut SDS-jäämät olivat selkeästi korkeampi kuin teoreettiset arvot. Tämä johtuu liukenemattoman kalsium dodekyyli sulfaatin $CaDS_2$ muodostumisesta, joka jää kuituverkostoon. SDS-jäämien määrä laski, kun veden kovuus laski, lämpötilaa nostettiin tai lisättiin nonionista surfaktanttia (Tween 20). Kationisen tärkkelyksen lisäys nosti SDS-jäämien määrää.

Tween 20 voitiin määrittää sekä HPLC-DAD-laitteella että spektrofotometrillä. HPLC-DAD:lla saatiin korkeampi tuloksia kuin spektrofotometrisellä menetelmällä, koska Tween 20 ei uuttunut täysin vedellä. Kun vettä, etanolia ja asetonia verrattiin uuttoliuottimina Soxhlet-uutossa, tulokset osoittivat selkeästi, että etanoli ja asetoni uuttivat enemmän Tween 20 -surfaktanttia kuin vesi. Tween 20 -jäämien määrän ei havaittu olevan teoreettisia arvoja suurempia.

PREFACE

This Master's thesis was done in co-operation with the University of Jyväskylä and VTT Jyväskylä as a part of a Future Fibre Products 2020 program. The thesis was done between October 2017 and August 2018. The experimental work was performed between October 2017 and April 2018. The literature references for this work were searched using mainly Google Scholar, Web of Science and VTT library search engines.

I would like to acknowledge my supervisors, Ph. Lic. Timo Lappalainen from VTT Jyväskylä, and Ph.D. Jarmo Louhelainen from the University of Jyväskylä, for the great guidance, advice, inspiration and encouragement during this work. Special thanks to Ph.D. Ari Väisänen, Ph.D. Hannu Pakkanen and research assistant Jouni Väli-Torala for the assistance and ideas with the analytical instruments. I would like to thank the technical research team of VTT Jyväskylä for all the help in practical laboratory work. I would also like to thank my spouse, family and friends. Your support and encouragement have been invaluable during this work.

Future Fibre Products 2020 is a jointly funded ERDF (European Regional Development Fund) project. The project started on 1.6.2017 and will end on 31.5.2020. The goal of the program is to develop new sustainable and value-added fibre based products for either replacing oil-based current products or to develop completely new fibre-based solutions for different sectors. Jani Lehto is the project owner at VTT and Tech. Lic. Harri Kiiskinen is the project manager.

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CONTENTS

ABBREVIATIONS

4-DBSA	4-Dodecylbenzenesulphonic Acid
AES	Alkyl Ethoxy Sulphate (or Alkyl Ether Sulphate)
AS	Alkyl Sulphate (or Alcohol Sulphate)
BfR	German Bundeinstitut für Risikobewertung (eng. Federal Institute for Risk Assessment)
CAS	Chemical Abstract Number
CLP	Classification, Labelling and Packaging (regulation)
CMC	Critical Micelle Concentration
CoE	the Council of Europe
CSAC	Critical Surface Association Concentration
DDAC	Didecyldimethylammonium Chloride
ECHA	European Chemicals Agency
EFSA	European Food Safety Authority
EINECS	European Inventory of Existing Commercial Chemical Substances
ELINCS	European List of Notified Chemical Substances
ELS	Evaporative Light Scattering
EO	Ethylene Oxide
FCM	Food Contact Material
EPA	Environmental Protection Agency
FDA	Food and Drug Administration
FDAMA	the Food and Drug Administration Modernisation Act

GHS	Globally Harmonised System of classification and labelling of chemicals
GMP	Good Manufacture Practice
GRAS	Generally Recognised As Safe
HPLC	High-Performance Liquid Chromatography
HPLC-DAD	High-Performance Liquid Chromatography equipped with Diode Array Detector
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
LAS	Linear Alkylbenzene Sulphonate
LLE	Liquid-Liquid Extraction
MAE	Microwave-Assisted Extraction
NLP	No Longer Polymers
NOAEC	No Observed Adverse Effect Concentration
NOAEL	No Observed Adverse Effect Level
NOEC	No Observed Effect Concentration
PBT	Persistent, Bio-accumulative and Toxic
PEC	Predicted Environmental Concentration
PLE	Pressurised Liquid Extraction
PNEC	Predicted No Effect Concentration
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RI	Refractive Index
SAX	Strong Anion Exchanger

SCX	Strong Cation Exchanger
SDS	Sodium Dodecyl Sulphate
SES	Solvent Extraction Spectrophotometry
SFE	Supercritical Fluid Extraction
SPE	Solid Phase Extraction
STP	Sewage Treatment Plant
TMP	ThermoMechanical Pulp
TSCA	Toxic Substance Control Act
vPvB	very Persistent and very Bio-accumulative
QAC	Quaternary Ammonium Compound
WAX	Weak Anion Exchanger
WCX	Weak Cation Exchanger

LITERATURE PART

1 INTRODUCTION

Surfactants are widely used in different fields of industry and household applications, e.g. as washing, foaming, emulsifying, dispersing and wetting agents.[1] Surfactants are produced worldwide over 10 million tonnes each year.[2] As surfactants are extensively used, a wide variety of determination methods for quality control purposes and environmental monitoring have been developed.[3]

Recently, the use of foam forming technology in papermaking have been started to re-investigate. In the foam forming process, fibres are dispersed in foam produced by surfactants. Foam forming technology may offer a more resource efficient way for papermaking and a possibility to create new kind of fibre products.[4] The ability to determine surfactants residues is important for the development of foam forming technology as it is directly related to the circulation of surfactant in the process but also because surfactant residues may effect on the properties of the foam-formed product.

The literature part of this thesis starts with a discussion about the basics of surfactants. The history and the present state of foam forming research are also briefly discussed. The main focus in the literature part is in the analysis methods of surfactants. Sample pre-treatment methods and the two most widely used techniques for the quantitative determination of surfactants are discussed, spectrophotometric and chromatographic methods. The potential of atomic spectroscopy is also briefly introduced. Finally, the legislation relating to chemical residues in paper and board and the toxicological concerns of surfactants are discussed.

The experimental part of this thesis concentrates on the determination of surfactant residues. Residues of an anionic surfactant, sodium dodecyl sulphate (SDS), and a non-ionic surfactant, Tween 20, from foam-formed samples were determined. In addition, determination of 4-dodecylbenzenesulphonic acid (anionic surfactant) in water solutions by UV spectrophotometry is discussed.

2 SURFACTANTS

Surfactants i.e. surface active agents are molecules that can reduce interfacial tension. Surface active properties arise from amphiphilic nature of surfactants meaning they have both polar and nonpolar character. Surfactant consists of a hydrophobic tail and a hydrophilic group at the end of the tail (in a solvent other than water terms lyophobic and lyophilic are used). The hydrophobic tail is comprised of a hydrocarbon chain that can be linear, branched or cyclic and it usually contains 8-18 carbon atoms. Hydrophilic group interacts with water via hydrogen bonding, dipole-dipole interaction or ion-dipole interaction whereas hydrophobic part avoids contact with water molecules. Due to this behaviour surfactants adsorb at interfaces and form organised structures. Surfactants are classified into four main classes according to the nature of the hydrophilic group: anionic, cationic, zwitterionic and non-ionic surfactants.[1,5,6] The nature of the polar group affects strongly on its surface active properties.

2.1 Surfactant types

Generally surfactants are classified according to the charge of the polar head group: anionic, cationic, zwitterionic and non-ionic surfactants. Zwitterionic surfactants have both positive and negative charge, and for some the state of ionisation is pH dependent. The counterion affects a lot on the solubility properties of the surfactant.

2.1.1 Anionic surfactants

Anionic surfactants are the most consumed surfactants as they cover approximately 70 % of the total consumption. They are used in different household detergent formulations and personal care products. Anionic surfactants can be divided according to hydrophilic head group into carboxylates, sulphates, sulphonates and phosphates. The most manufactured anionic surfactants are linear alkylbenzene sulphonates (LAS), alkyl ethoxy sulphates (AES) and alkyl sulphates (AS).[1,7] Examples of common anionic surfactants are presented in Table 1.

Traditional soap used in soap bars is the largest single type of anionic surfactant used.[6] Soaps are sodium and potassium carboxylates, which are manufactured by saponification from fatty acid mixtures obtained from e.g. tall oil, coconut oil and palm oil. The problem with carboxylates is their precipitation in hard water. This can be solved by making the surfactant more hydrophilic. Other types of carboxylates that are more compatible with electrolytes are ethoxy carboxylates, ester carboxylates and sarcosinates.[1,5]

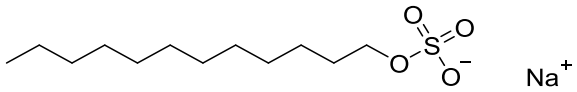
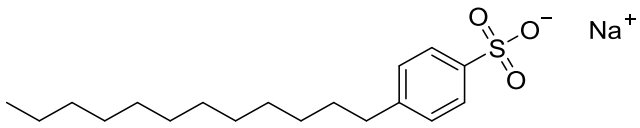
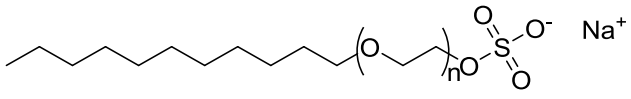
Sulphate surfactants can be made from alcohols, triglyceride oils and fatty acids. Alcohol sulphates (AS) are produced by sulphating alcohol using SO_3 or chlorosulphonic acid. Alcohol

sulphates show excellent foam forming properties but they cannot be used in hard water. They are also susceptible to hydrolysis especially in acidic conditions. Electrolyte compatibility and chemical stability can be improved by ethoxylation.[1]

Sulphonates are a good alternative for sulphates as they are chemically stable due to less polarised carbon-sulphur bond. There is a wide variety of different sulphonate surfactants. The most common type of sulphonate surfactants are linear alkyl benzene sulphonates (LAS). LAS are usually prepared by reaction of sulphuric acid with alkyl benzenes.[1,5] LAS are compatible with hard water but they may cause skin irritation. Compared with LAS, paraffin sulphonates and α-olefin sulphonates are less irritating to skin, more water soluble and have better biodegradability.[1]

Common phosphate surfactants are sodium alkyl phosphates and phosphoric acid esters produced from polyoxyethylenated (POE) alcohols and phenols.[1]

Table 1. Examples of anionic surfactants. The surfactant name, structure, CAS number, molecular formula and molecular weight are presented.

Surfactant name, structure and CAS number	Molecular formula	MW (g/mol)
Sodium dodecyl sulphate (SDS) CAS: 151-21-3 	$C_{12}H_{25}OSO_3Na$	288.38
Sodium dodecylbenzene sulphonate CAS: 25155-30-0 	$C_{18}H_{29}SO_3Na$	348.48
Sodium laureth sulphate CAS: 9004-82-4 	$CH_3(CH_2)_{11}(O\ CH_2\ CH_2)_nOSO_3Na$	420.54*

* Typically n = 3

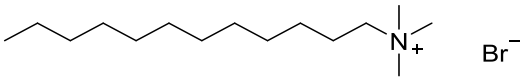
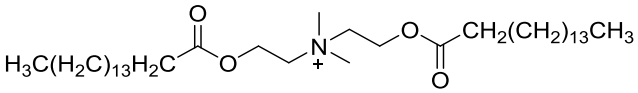
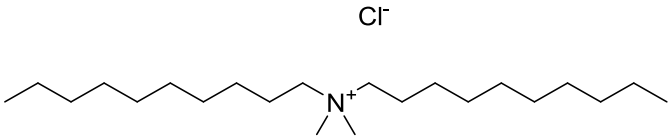
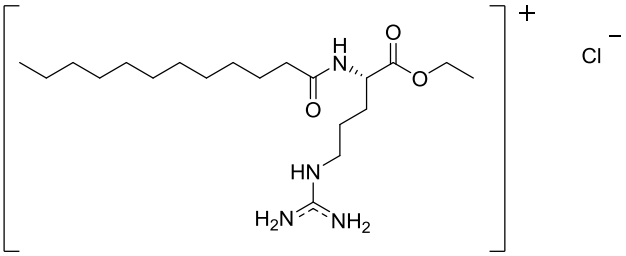
2.1.2 Cationic surfactants

In cationic surfactants, the hydrophilic group carries a positive charge. Majority of the cationic surfactants used are long-chain amines or quaternary ammonium compounds (QACs). Table 2 shows examples of cationic surfactants. Halides or sulphates are used as counterions. Amine-

based surfactants must be in a protonated state to function, so they cannot be used in alkaline conditions. Because of the stability in acidic solutions, amine-based surfactants are used as corrosion inhibitors and as emulsifying agents in acidic emulsions. QACs have the general structure of $R_1R_2R_3R_4N^+X^-$. Unlike amines, QACs are unaffected by pH-changes. In QACs, there may be more than one long alkyl chain. Common cationic surfactants of this class are e.g. alkyl trimethyl ammonium salts, dialkyl dimethyl ammonium salts, alkyl ester ammonium salts and imidazolinium derivatives. Nowadays, diester QACs are used in fabric softeners. They replaced dialkyl QACs because esters are easily hydrolysed which makes the surfactant readily biodegradable.[1,6]

Cationic surfactants can be used in hard water and with non-ionic and zwitterionic surfactants, but they are incompatible with anionic surfactants. Since many natural and synthetic surfaces are negatively charged, many of the applications of cationic surfactants are based on the adsorption of the surfactant at solid surfaces. Cationic surfactants are used e.g. as softening agents in fabric softeners, antistatic agents in hair conditioners, corrosion inhibitors, ore flotation collectors and anticaking agents in fertilizers.[1,6]

Table 2. Examples of cationic surfactants. The surfactant name, structure, CAS number, molecular formula and molecular weight are presented.

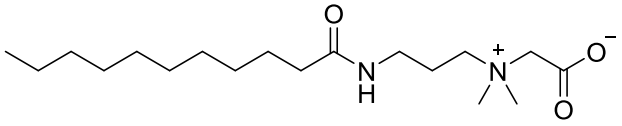
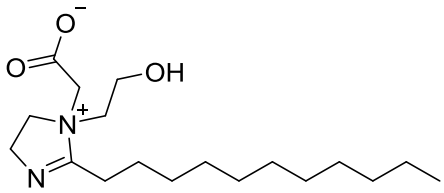
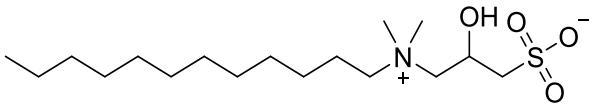
Surfactant name, structure and CAS number	Molecular formula	MW (g/mol)
Dodecyltrimethylammonium bromide CAS: 1119-94-4 	$C_{15}H_{34}BrN$	308.35
Dipalmitoylethyl dimonium chloride CAS: 97158-31-1 	$C_{38}H_{76}ClNO_4$	646.48
Didecyldimethylammonium chloride (DDAC) CAS: 7173-51-5 	$C_{22}H_{48}ClN$	362.08
Ethyl lauroyl arginate hydrochloride CAS: 60372-77-2 	$C_{20}H_{41}ClN_4O_3$	421.02

2.1.3 Zwitterionic surfactants

Zwitterionic surfactants possess hydrophilic groups that have both a positive and a negative charge. Common zwitterionic surfactants show structural similarity with amino acids and contain a quaternary nitrogen group and a carboxylate group.[1,6] Most of the zwitterionic surfactants are pH-sensitive i.e. they change the state of ionisation with pH. Therefore, surface active properties are also pH-dependent. At isoelectric point, both ionic groups of the molecule are equally ionised and the overall charge is zero. The solubility of the surfactant is the lowest at isoelectric point. In alkaline solution, pH-sensitive zwitterionics show features of anionic surfactants and in acidic solutions features of cationic surfactants. pH-sensitive zwitterionics include e.g. N-alkylbetaines, amidoamines, amidobetaines, imidazoline carboxylates and β-N-alkylaminopropionic acids. Sulphobetaines, also referred to as sultaines, contain a sulphonate

group instead of the carboxylate group. They are pH-insensitive which means they are zwitterionic at the whole pH-range. Zwitterionic surfactants are very mild to the skin and eyes and therefore they are used e.g. in shampoos, cosmetics and fabric softeners.[1] They are used to reduce the irritation effects of anionic surfactants in shampoos.[8] Like non-ionics, zwitterionics can also be used together with all other types of surfactants and in high electrolyte concentrations.[6] Examples of common zwitterionic surfactants are presented in Table 3.

Table 3. Examples of zwitterionic surfactants. The surfactant name, structure, CAS number, molecular formula and molecular weight are presented.

Surfactant name, trade name, structure and CAS number	Molecular formula	MW (g/mol)
Cocoamidopropyl betaine CAS: 4292-10-8 	$C_{19}H_{38}N_2O_3$	342.52
Sodium lauroamphoacetate Trade name: Miranol® Ultra L-32E CAS: 15608-14-7 	$C_{18}H_{34}N_2NaO_3$	349.47
Lauryl hydroxysultaine Trade name: Betadet® S-20 CAS: 13197-76-7 	$C_{17}H_{37}NO_4S$	351.55

2.1.4 Non-ionic surfactants

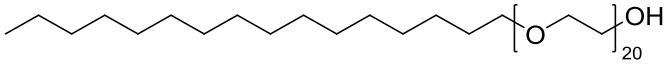
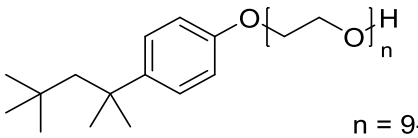
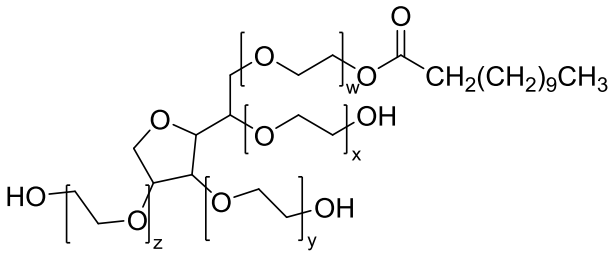
In non-ionic surfactants, the hydrophilic part is an uncharged polyethyleneoxide or polyhydroxyl chain.[6] Non-ionic surfactants are the second largest type of surfactant manufactured and there exist several different classes of non-ionics derived from different starting materials. The advantages of non-ionic surfactants are the compatibility with all other types of surfactants, electrolytes and hard water. Commercial non-ionic surfactants are often viscous liquids or pastes and the purity is poor, as there is a wide distribution of different POE

chain lengths. Non-ionic surfactants are used as detergents, emulsifiers, wetting agents and dispersing agents e.g. in cleaning products, laundry detergents, cosmetics, pulp and paper products and paints. Generally, they have a low foaming character which can be utilised in certain products.[1] Examples of non-ionic surfactants are shown in Table 4.

Polyethyleneoxide non-ionics contain ethyleneoxide (EO) units, typically 5-10 moles, and they are prepared by base catalysed polymerisation reaction of ethylene oxide. Common polyether non-ionics are alcohol ethoxylates, fatty acid ethoxylates, alkylphenol ethoxylates and fatty amine ethoxylates. Alcohol ethoxylates can be considered as the most important type of non-ionic surfactants. They are often abbreviated using formula C_mE_n where *m* is the number of carbon atoms and *n* is the number of EO units in the surfactant. Fatty amine ethoxylates can be categorised both into cationic and non-ionic surfactants. When the number of EO units is large, fatty amine ethoxylates can be considered as non-ionic surfactants.[6]

Polyhydroxy non-ionics include, e.g. propylene glycol esters, sorbitan esters, alkyl polyglucosides and polyglycerol esters, and their corresponding ethoxylated derivatives. Sorbitan esters (also known as Spans) are prepared from sorbitol and a fatty acid. Sorbitol dehydrates forming a five-membered ring after which esterification with the fatty acid takes place. Spans and their ethoxylated derivatives (also known as Tweens) are food grade surfactants and they are used e.g. as emulsifiers in foods and pharmaceuticals.[1,6]

Table 4. Examples of non-ionic surfactants. The surfactant name, structure, CAS number, molecular formula and molecular weight are presented.

Surfactant name, trade name, structure and CAS number	Molecular formula	MW (g/mol)
Polyoxyethylene (20) cetyl ether Trade name: Brij® 58 CAS: 9004-95-9 	$C_{56}H_{114}O_{21}$	1123.51
Polyethylene glycol *tert*-octylphenyl ether Trade name: Triton™ X-100 CAS: 9002-93-1  n = 9-10	$(C_2H_4O)_nC_{14}H_{22}O$	~625
Polyoxyethylene (20) sorbitan monolaurate Trade name: Tween® 20 CAS: 9005-64-5  w+x+y+z = 20	$C_{58}H_{114}O_{26}$	1 227.54

2.1.5 Gemini surfactants

Increasing use of surfactants has led to an interest in designing another type of surfactants. One new class of synthetic surfactants that are studied are gemini surfactants.[9] Gemini surfactant consists of two surfactant monomers connected by a spacer between the hydrophilic head groups or near them. Gemini surfactants can also be referred to as dimeric surfactants. Usually the two surfactant monomers are identical but also heterogemini surfactants, having two different surfactant monomers, have been synthesised. Cationic alkylammonium gemini surfactants are the most studied. They can be synthesised by reacting trisubstituted amine with α,ω-dihalocompound.[6] The general structure of a gemini surfactant is presented in Figure 1.

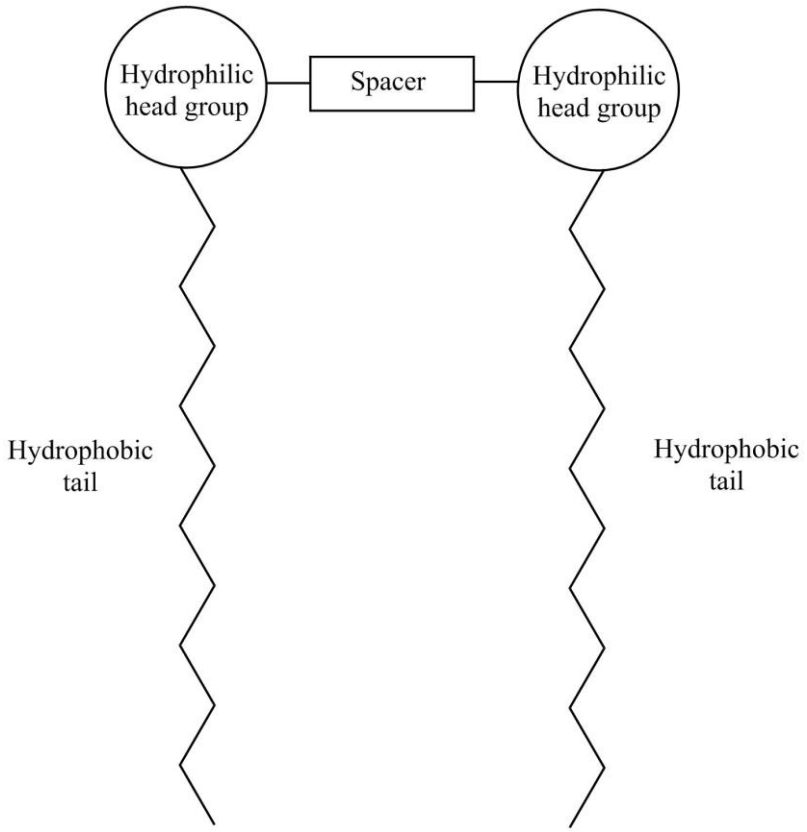


Figure 1. The general structure of a gemini surfactant. Two surfactant monomers are linked by a spacer.

Gemini surfactants have unique properties that have raised interest in many applications. The critical micelle concentrations (CMCs) are much lower for gemini surfactants than for the corresponding surfactant monomers. Gemini surfactants are also more effective in lowering the surface tension, so they can be used in lower concentration compared to surfactant monomers to gain the same surface tension reduction.

The choice of spacer defines to a large extent the surface activity properties of the gemini surfactant. The spacer can be hydrophobic or hydrophilic and flexible or rigid. Rigidity can be gained by introducing double or triple bonds and phenyl groups.[9] By varying the length of the spacer, the CMC can be controlled which in turn affects e.g. on the foamability of the gemini surfactant.[9,10]

2.2 Adsorption of surfactants at interfaces

Surfactant adsorption can be seen as partitioning between the surface/interface and the bulk solution. The amount of surfactant adsorbed is dependent on surfactant concentration. Adsorption isotherms describe the amount of surfactant adsorbed at the surface/interface as a

function of the surfactant concentration in the bulk solution.[6] The efficiency of adsorption describes the amount of surfactant adsorbed at a certain equilibrium concentration of the bulk solution. The effectiveness of adsorption describes the total amount of surfactant that can be adsorbed at the surface i.e. the surface saturation concentration. Surface excess concentration Γ describes the amount of surfactant adsorbed per unit area at an interface.[1]

Interfacial or surface tension γ is the minimum free energy that is required to increase the area of an interface by unit area. The interface is the boundary between two immiscible phases. When the other phase is air, the term surface is used. Interfacial tension arises from the fact that the molecules at an interface have higher potential energies.[5] The surface tension of pure water is 72 mN/m.[9] Surfactants lower the surface tension, and values of 30-40 mN/m can be reached depending on the nature of surfactant. At the interface between air and liquid water, surfactants adsorb onto the surface by orienting the hydrophilic part towards the liquid and the hydrophobic part pointing towards the air.[5]

There are several mathematical models that describe the adsorption at air/liquid and liquid/liquid interfaces, but generally the Gibbs adsorption equation is used. All the models are based on relating the surface concentration of a surfactant to the change in the surface or interfacial tension. According to Gibbs model, there is a thermodynamic relationship between interfacial tension γ and surface excess Γ. According to Gibbs-Deuhem equation

$$\mathrm{d}G^{\circ} = -S^{\circ}\mathrm{d}t + A\mathrm{d}\gamma + \sum n_{\mathrm{i}}\mathrm{d}\mu_{\mathrm{i}}, \quad (1)$$

where G° is the surface free energy, $S^{\circ}$is the entropy, A is the area of the surface, n_{i} is the number of moles of component i and μ_{i} is the chemical potential of that component. In the Gibbs model, adsorption is considered as an equilibrium process.[1,5]

Surfactants tend to adsorb at solid surfaces from aqueous solutions. Depending on the nature of the surfactant and the solid adsorbent, there are several different mechanisms through which the adsorption can happen. Adsorption can happen e.g. via ion pairing, hydrogen bonding, Lewis acid-Lewis base interaction, dispersion forces and hydrophobic bonding.[1]

Often surfactants show Langmuir-type adsorption behaviour at solid/liquid interfaces. The Langmuir adsorption equation is

$$\Gamma_1 = \frac{\Gamma_{\mathrm{m}} C_1}{C_1 + a}, \quad (2)$$

where Γ_{m} is the surface concentration (mol/cm^2) at monolayer adsorption, C_1 is the surfactant concentration (mol/l) in the aqeous solution at adsorption equilibrium and a is a constant. Adsorption at solid/liquid interface is usually described by the adsorption isotherm which shows the amount of surfactant adsorbed (per unit mass or unit area) as a function of the bulk surfactant concentration in the liquid phase.[1]

The driving force for adsorption at hydrophobic surfaces is minimising the contact between the hydrophobic tail and the aqueous environment. Adsorption at hydrophilic surfaces is driven by other forces.[6] The adsorption isotherm for the adsorption of surfactant at hydrophilic surface, is typically S-shaped and there are four different regions (see Figure 2). In region I the adsorption is weak, and the amount of surfactant adsorbed increases linearly with concentration. The surfactant adsorbs as single molecules. At certain equilibrium concentration, the adsorption increases suddenly (region II). This break point is called the critical surface association concentration (CSAC). The increase in adsorption is due to the formation of surfactant aggregates at the solid surface. At higher concentrations, surfactants start to self-assemble at the surface. In region III the adsorption weakens, and ideally the surface concentration should reach its maximum at the CMC (critical micelle concentration) after which the surface concentration does not change anymore.[6,11] However, a decrease in the extent of adsorption after the reaching the maximum has also been observed in the case of adsorption of anionic surfactants at the cellulosic surface (see Figure 2).[11]

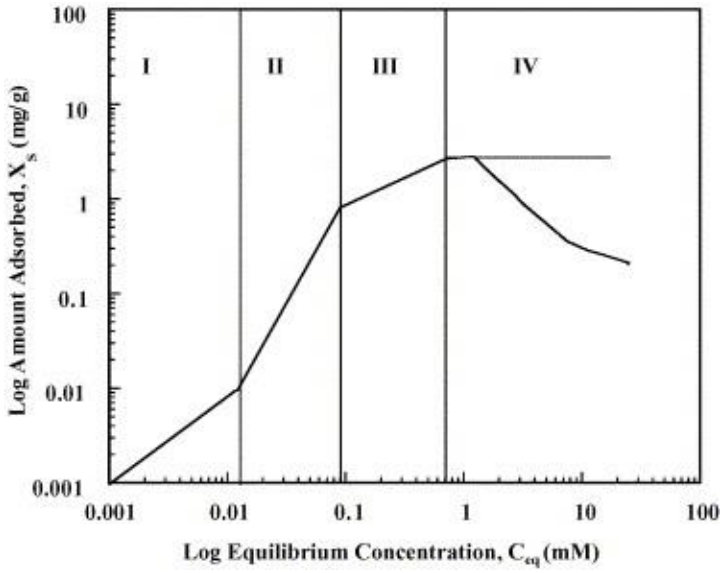


Figure 2. A log-log plot of adsorption isotherm describes the adsorption of surfactants at the solid-liquid interface. Reprinted with permission from[11]. Copyright (2005) Elsevier.

2.3 Physicochemical properties of surfactants

Amphiphilic molecules have a feature of forming self-assembled structures. As the concentration of surfactant rises, instead of accumulating at interfaces, surfactants start to form clusters to minimise the contact between hydrophobic parts and water. These clusters are called micelles. In aqueous media micelles are formed so that hydrophobic parts are oriented toward the interior of the micelle and hydrophilic groups are on the surface.[1,5] An illustration of a spherical micelle structure is presented in Figure 3. The hydrophobic core is surrounded by a Stern layer that consists of the hydrophilic groups and counterions that neutralise the charge (see Figure 3). The outermost layer is a diffuse layer of counterions called a Gouy-Chapman electrical double layer. If a surfactant has EO units, water molecules enter into the micelle interacting with the EO units forming a palisade layer.[12] Micelles can be spherical, cylindrical or lamellar in shape. The shape can be predicted by calculating the critical packing parameter. The size and shape of a micelle depend e.g. on the temperature of the solution, the structure of the surfactant, surfactant concentration and the present electrolytes and other additives. In general, can be said that in aqueous media surfactants with long and linear hydrophobic groups and bulky loosely packed hydrophilic groups tend to form spherical micelles containing 50-100 surfactant molecules.[1,5]

The concentration at which surfactants start to form micelles is the critical micelle concentration, abbreviated as CMC. Many physical properties, like surface tension, light scattering and conductivity of a surfactant solution change drastically as a function of surfactant concentration but reach maximum or minimum at the CMC. These changes in physical properties can be used to determine the CMC. For example, the surface tension reaches its minimum at the CMC. After reaching the CMC surface tension remains nearly constant. CMC is affected by e.g. alkyl chain length, type of the hydrophilic group and the presence of electrolytes. Typically CMC of non-ionic surfactants is much lower than for ionic surfactants. Alkyl chain length has the major effect on the CMC. As the alkyl chain length increases, the solubility of the surfactant monomer decreases and the CMC decreases as well.[6] Bulky groups and carbon-carbon double bonds generally increase the CMC due to steric hindrance.[1] Introducing hydrophilic EO units increases the CMC slightly. Counterions affect the CMC, because they stabilise micelles with electrostatic interactions. Change in the valency of counterion from monovalent to divalent leads to decrease in the CMC.[6]

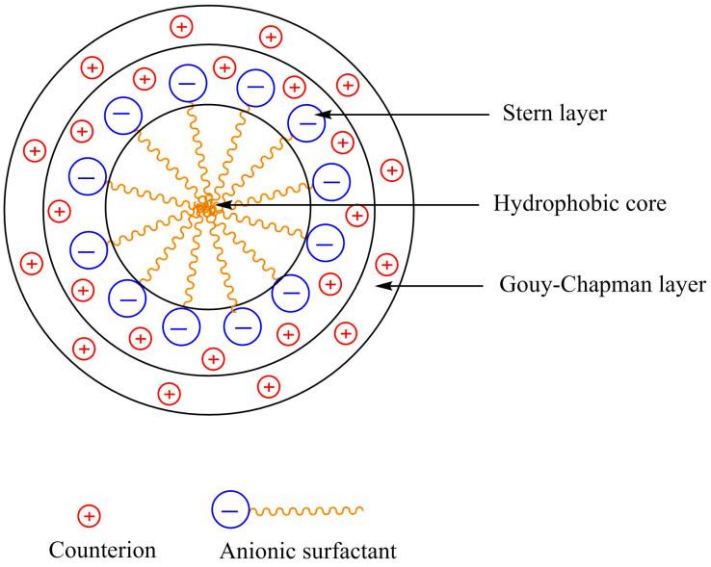


Figure 3. The structure of a spherical micelle consisting of anionic surfactants.

Micellisation is utilised in solubilisation where the material is dissolved by the interaction with micelles. This phenomenon is useful particularly in the case of materials that are otherwise insoluble in the solvent, e.g. detergency is based on solubilisation by micelles. A material solubilises within a micelle into the inner core, palisade layer or on the surface depending on the type of interaction and the nature of the material and the surfactant. Aliphatic hydrocarbons and other nonpolar molecules solubilise into the inner core whereas small polar molecules are located near the surface.[1]

Temperature affects greatly on the physical properties of surfactants. Krafft temperature T_k is the temperature where solubility becomes equal with CMC. At Krafft temperature the solubility of surfactant rises drastically because of micelle formation. Usually Krafft phenomenon is observed for ionic surfactants. If a surfactant is used below its Krafft temperature, no micelles can form because the solubility is below CMC. Also the maximum reduction in surface tension cannot be reached. Figure 4 shows a graph that describes Krafft phenomenon. CMCs of non-ionic surfactants are much more temperature dependent than for ionic surfactants. Furthermore, the CMCs of non-ionics decrease with increasing temperature. This is believed to be caused by a higher portion of high energy conformations in the POE chain. Due to these higher energy conformations there are fewer possibilities for hydrogen bonding i.e. the surfactant becomes less polar.[6] The temperature, where a water solution of non-ionic surfactant starts to scatter light and becomes turbid, is called the cloud point. “The cloudiness” of the solution arises from the phase separation of the solution. As the temperature of the solution rises, micelles grow and the repulsion between micelles decreases leading to phase separation. The solution is separated into a dilute solution containing only surfactant unimers and a concentrate micellar phase. At a

concentration of a few percents the phase separation occurs fairly at a constant temperature.[1] Normally the cloud point is defined for 1 % surfactant solutions.[6]

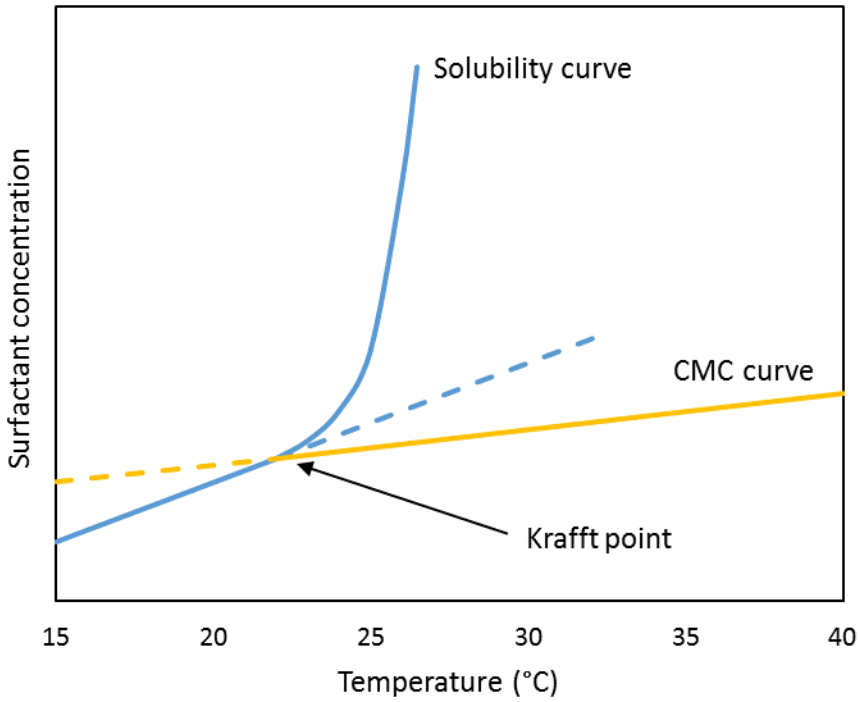


Figure 4. Description of Krafft point. The solubility of a surfactant rises gradually as temperature increases. The temperature where the solubility reaches CMC is called Krafft point. When the temperature rises above Krafft point, the solubility increases strongly because of the surfactant pack into micelles.

3 FOAM FORMING TECHNOLOGY

3.1 Foams

Foams are present in many applications used every day, e.g. in cleaning and personal hygiene products but also in foods and elastic materials such as memory foam. Foams are utilised in many industrial applications, e.g. in de-inking of recycled newspaper, in mineral flotation and in the dyeing of textiles.[13] There are liquid and solid foams. In liquid foams, gas is dispersed in a liquid phase and solid foams, gas is dispersed in solid material.[14] Here, only the liquid foams are discussed.

Liquid foams are dispersions of gas in liquids. Because pure liquids do not foam, foaming agents are needed to produce foams. In most applications, e.g. for detergent purposes, synthetic surfactants are used to generate foam. Surfactants adsorb at the gas-liquid interface and create elastic films stabilising the air bubbles. In food applications, proteins act as foaming agents.[10] Foam is commonly generated by mechanical mixing or by introducing gas through a nozzle into the liquid.[13]

The liquid fraction ϕ is the ratio between the volume of the liquid and the volume of foam. Foams are polydisperse, meaning that there is a range of different bubble sizes and shapes. As the liquid fraction in the foam decreases, the amount of liquid in the channels separating the bubbles decreases, and the bubbles become more regular in shape. Depending on the liquid fraction, foams can be considered as wet or dry foams. In wet foams, the liquid fraction is larger and the gas bubbles are nearly spherical whereas in dry foams, the gas bubbles are polyhedral in shape.[10] The critical liquid content of liquid foam ϕ_c, where the shape of the bubble is thought to change from polyhedral to spherical, is around 37 %. When the liquid content is above the critical value, the system is not considered anymore as foam but as a bubbly liquid in which the bubbles are separate and free to move. This transition is also called *the jamming transition*. Figure 5 presents, how the nature of foam changes as a function of liquid content.[14]

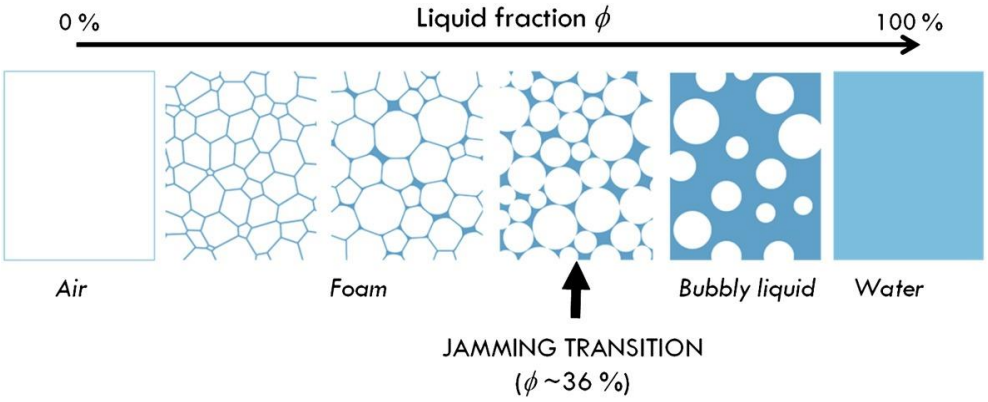


Figure 5. The shape of foam bubbles for different liquid fractions.[14]

Liquid foams are thermodynamically unstable so eventually foams collapse. The liquid drains through the Plateau borders, which are the borders where liquid lamellae of gas bubbles meet. According to Plateau rules, the foam network has a tetrahedral arrangement. Any three bubbles that are in contact are separated by four borders that join in a tetrahedral arrangement (Figure 6). The intersection where the four borders meet is node.[10]

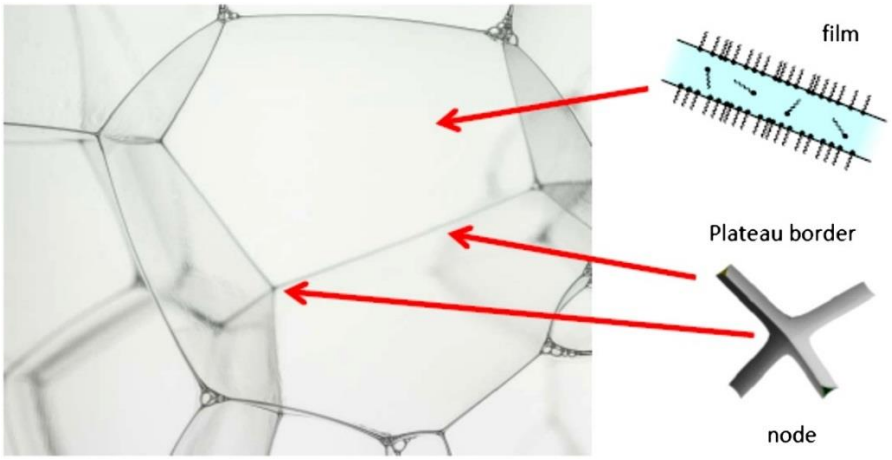


Figure 6. Picture of an aqueous dry foam showing the Plateau borders and nodes.[14]

Foam is frequently characterised by foamability and foam stability. Foamability refers to ease of foam generation and is often assessed by the initial foam height or volume immediately after foam generation. Foam stability i.e. the lifetime of the foam can be measured e.g. by static tests, in which the foam is allowed to collapse after the foam generation and change in foam height or volume is measured. Foamability depends e.g. on the energy input, the viscosity, the dimensions of the vessel and the type and concentration of surfactant.[10]

Many standardised test methods for characterising foamability and foam stability exist but they differ on how the foam is generated. Therefore, foamability and foam stability depend highly on the test method, but even on the surrounding environment (humidity, temperature etc.). Frequently used test method for characterising foamability and foam stability is the Ross-Miles test (pour test). In the method, a portion of the surfactant solution is allowed to fall from a pipette into a cylindrical vessel containing the same surfactant solution at a temperature of 60 °C. The foam is generated by the impingement of the solutions. Foamability and foam stability are interrelated. Based on the Ross-Miles test surfactant systems can be divided into five regions.[10] Unique tests for foamability and foam stability have been developed in different fields of industry to study the foaming for example in beer or shampoos.[10]

More detailed information about foam properties can be obtained from the air content and the bubble size distribution as they determine e.g. viscosity, stability and drainage of foam.[13] Various imaging techniques have been developed to determine the bubble size distribution in liquid foams including 2D imaging, optical fibre probe analysis, nuclear magnetic resonance imaging, ultrasonic imaging and laser light scattering techniques.[10] Optical imaging has been the most commonly used technique.[13] 2D imaging is often performed by placing the foam inside a narrow glass cell.[10,13]

3.2 General about papermaking

Papermaking industry has changed a lot since the 1950s. In 2010, packaging papers and boards formed over half of the world paper production. Also customers' requirements have changed. High-quality products with low price and more suitable for the end use are wanted. As most of the production costs is formed by fibre raw material procurement, the amount of fibres in the product is minimised. For these reasons, there is an increasing need to improve the resource efficiency and decrease the water and energy consumption in the papermaking process.[15]

Papermaking process includes the following steps: preparation of the fibre stock, sheet or web forming, wet pressing, drying, sizing and smoothing. First, the fibre stock is prepared by disintegrating the fibre material into water. Either primary or secondary i.e. recycled fibres can be used. Primary fibres come from the chemical or mechanical pulp. The quality of fibres affects strongly on how many unit operations are involved. Recycled fibres demand more preparation steps. Interfering substances are separated from the suspension e.g. by flotation. Fillers and coating colours can be added during stock preparation, during the delivery to the paper machine or not until the stock is delivered to the paper machine. The prepared suspension is delivered to the paper machine, which produces a fibre web from the stock. Figure 7 shows the structure of a typical fourdrinier paper machine. A paper machine consists of forming, pressing, drying, and calendaring sections. The suspension is delivered to the headbox, which distributes the suspension uniformly on to a moving wire. After forming, the web is pressed and the residual amount of water is removed by heat. The purpose of calendaring is smoothen the surface of the paper. Finally, the paper web is reeled into rolls. As the manufacturing process proceeds from the wet end (forming section) to the dry end (calendaring section), the dry matter content changes from about 1.2 % to 92 %. A paper machine can be up to 600 m long and 10-11 m wide. Today, the maximum machine speed of the paper machine is 950-2200 m/min depending on the paper grade produced.[15]

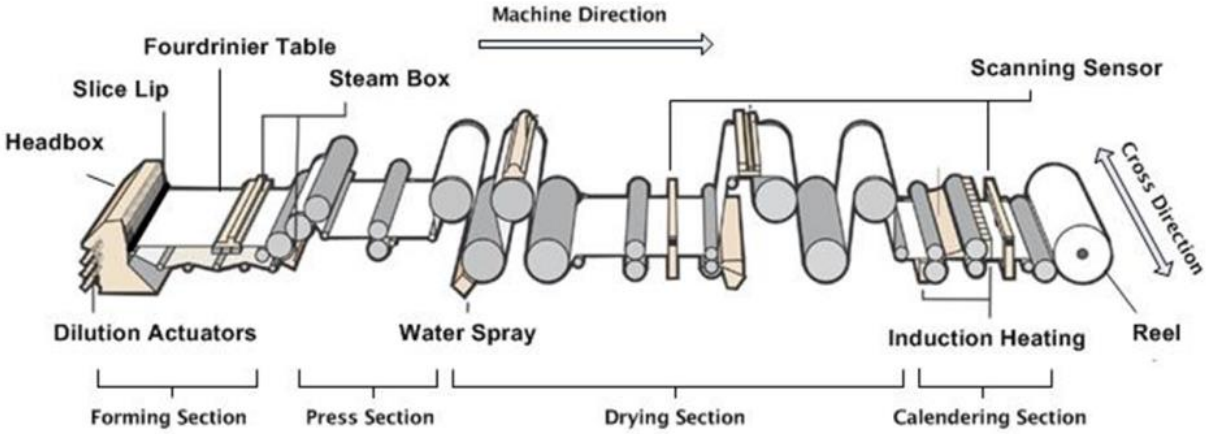


Figure 7. The structure of a typical fourdrinier paper machine.[16]

3.3 Foam forming

The traditional papermaking process is not suitable for handling of long fibres, which are used e.g. in the manufacture of nonwovens. As fibres experience high shear forces, they start to rotate and form bundles i.e. flocs. Fibre flocculation results in non-uniform distribution of fibres. Uniform and layered structure of the formed sheet is a prerequisite for gaining e.g. good strength and surface properties. There are two solutions to fibre flocculation. One way is to reduce the fibre consistency below the critical value, where the fibres start to flocculate. Another way to control the fibre flocculation is to increase the viscosity of the transferring medium. Increased viscosity restricts the movement of fibres and thus reduces collisions of fibres. The viscosity can be increased by adding e.g. natural gums to the fibre suspension. This approach was known already in the beginning of papermaking history. However, handling of long fibres demands a remarkable increase in viscosity, which results in slow drainage and therefore slow production speed.[17]

Foam forming technology provides a promising alternative to the traditional water-laid papermaking process. The technology was invented already in the beginning of 1970s by Radvan *et al.* at the Wiggins Teape Research and Development. Back then, it was called the Radfoam process. The process was developed especially for the needs of the nonwoven industry but it was discovered that the process could be applicable also to papermaking.[17] The development of foam forming technology for papermaking applications proceeded to a pilot scale in the mid-1970s, but the technology was not widely applied in paper industry. Water forming has remained the dominating technology in papermaking.[18] Nowadays, foam forming

is used in nonwoven applications, e.g. in the manufacturing of filter materials and technical textiles.[4]

In the foam forming process, the flocculation problem is overcome by dispersing fibres in aqueous foam instead of water. The foam is generated by using surfactants, and it has properties of the wet foam. The suitable air content of the foam-fibre mixture is typically 60-75 % and the foam contains spherical air bubbles having diameters of 20-150 µm. This kind of foam-fibre mixture behaves like a pseudoplastic fluid. Pseudoplastic fluid exhibits low viscosity under high shear conditions and high viscosity under low shear conditions. This means that during the stock preparation and the formation of the web, viscosity of the foam is low which enables uniform distribution of fibres. During the stock transfer, where there is no turbulence involved, the viscosity is significantly higher. Flocculation is prevented by the high viscous forces but also by the air bubbles, which space fibres farther from each other. The usage of foam enables delivering of fibre stocks having higher consistencies, from 0.5 to 1.5 % (w/w).[17]

The experiments made in the 1970s showed, that more uniform structure could be gained by foam forming. The improved formation was evident especially when using long fibres. The improved formation was observed visually and by measuring the variation in mass density distribution.[19–21] When compared with commercial papers, the foam-formed paper had the lowest variation in mass density distribution even if the fibre length was the highest.[20] Uniform structure contributes directly to optical, strength and surface properties of the paper. The uniform structure also means smoother surface so that fewer coating may be needed.[21] It was also noticed that foam-formed sheets had increased bulk and porosity compared to water-formed sheets at the same basis weight. This is explained by the presence of air bubbles. The air bubbles space fibres farther and a multi-layered fibre-bubble structure is formed. If the sheet is not pressed, the bubbles persist and as the foam-laid sheet is dried, the bubbles dry out and leave pores in the structure.[17,20]

Smith *et al.*[20] studied the tensile properties of water-formed and foam-formed sheets made in laboratory scale. It was observed that in both cases surfactant addition resulted in strength loss. When fibres were dispersed in water and surfactant was added without foaming the suspension, the tensile strength of the resulted hand sheets was decreased to less than half when compared to corresponding water hand sheets. The hand sheets made in surfactant solution also had a greater bulk compared to water hand sheets. When the sheets were prepared with foam, a further decrease in tensile strength and an increase in bulk were observed. However, the strength loss was regained by wet pressing to a level similar to the water hand sheets. Therefore, the strength

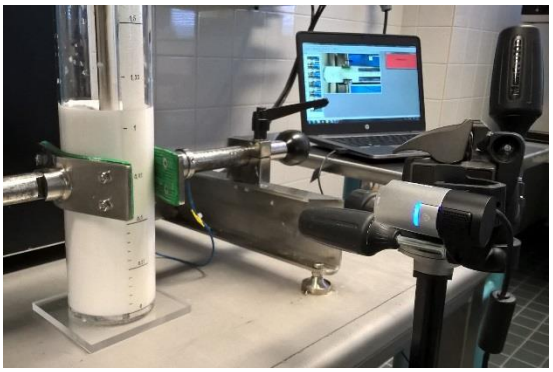
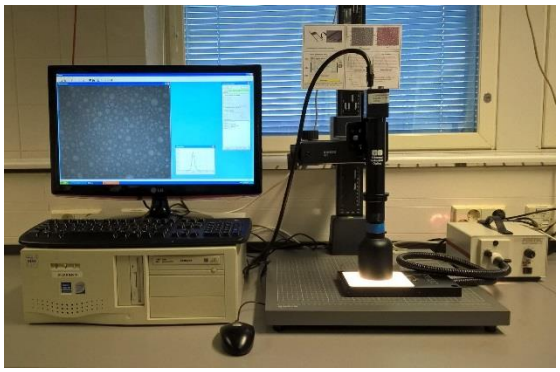
loss was not believed to be related to chemical interactions between the surfactant and fibres. The strength loss was explained by the reduced surface tension and the presence of air bubbles. The bonding between fibres are explained by so-called Campbell forces which draw the fibres close enough to each other. When the surface tension is reduced, the Campbell forces decrease and there are fewer fibres that can reach each other to bond. Also, the air bubbles space fibres more away from each other.

After a few decades of silence in the research of foam forming, the technology is being re-investigated. VTT Technical Research Centre of Finland has built a pilot-scale research environment for foam forming applications. The research environment enables both water-laid forming and foam-laid forming studies and the development of new kind of fibre products. The facilities also include laboratory-scale forming devices and equipment for characterisation of fibre-foam mixtures. The pilot environment is presented in Figure 8 and the laboratory scale research equipment in Figure 9.

Figure 8. The pilot environment for foam forming studies in VTT Technical Research Centre of Finland.

Lehmonen *et al.*[4] have studied the properties of the water-laid and foam-laid paper produced on a semi-pilot scale. The studies confirmed the observations of more uniform formation and enhanced forming consistency made in the 1970s. In addition, 63 % higher forming consistency could be used in the foam-laid paper to produce the same tensile strength as in water-laid paper and the specific β-formation was improved 69 %. The strength properties of water-laid and foam-laid paper at different grammages were compared. The tensile index of foam-laid paper

remained almost constant at all grammages whereas for water-laid paper, the tensile index started to decrease at the grammage below 45 g/m^2. This is because of the more uniform structure of the foam-laid paper. However, the z-directional strength of foam-laid paper was weaker. This is due to the larger pores in the foam-laid paper.

a)  b) 

c) 

Figure 9. Laboratory scale equipment for foam forming studies: a) The set-up for foamability and drainage studies, b) an imaging instrument for the determination of bubble size distribution and c) a foam hand sheet mould.

Foam forming serves a resource efficient way to produce paper and board products. Due to the possibility to use higher forming consistencies and efficient dewatering, the consumption of water can be reduced and less energy is needed in drying. Because of the better formation, lighter-weight products could be manufactured and savings in fibre raw material could be achieved.[4] Foam forming also enables usage of new kinds of raw materials, such as flexible long fibres and nanomaterials. This offers the possibility to develop new kind of fibre-based products.[13]

3.3.1 Bulky structures by foam forming

Typically, the structure of a paper sheet or a nonwoven product is layered and fibres are oriented in the in-plane direction (machine direction). By utilisation of foam forming, it is possible to orient fibres also in the out-of-plane direction (Z-direction) and to produce bulky and highly porous structures. With the same amount of fibres, a bulk close to 100 times higher has been achieved compared to conventional paper sheets. In these kind of low-density 3D fibre structures, there are more connections between fibres. Figure 10 shows an example of a low-density 3D fibre structure made by foam forming. Bulky structures having low density, of about 5 kg/m^3, possess extremely low stiffness i.e. they are soft structures. Tensile strength in the MD direction is low compared to conventional paper sheets, because there are fewer fibres oriented in that direction. However, the compression behaviour of low-density 3D fibre structures is unique. Because fibres oriented in the Z-direction are allowed to bend, high compressibility with little pressure can be gained. 3D fibre structures are also able to recover from the deformation.[22]

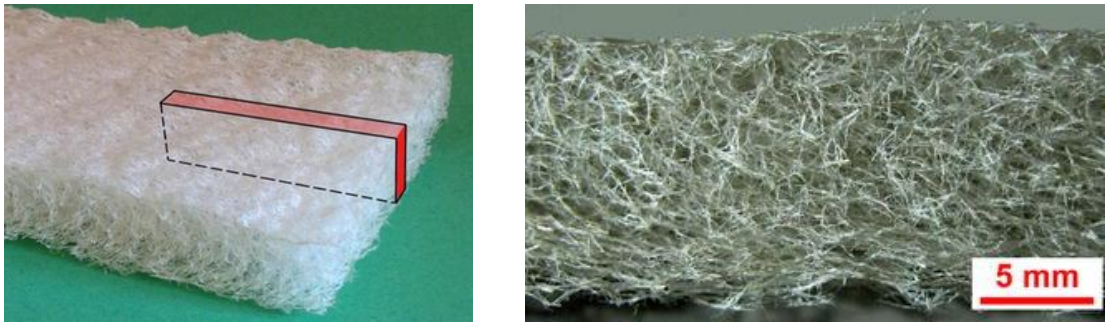


Figure 10. A bulky and porous structure made by foam forming. The cross-section on the right shows that wood fibres are randomly oriented.[22]

To produce bulky structures from wood fibres, dewatering processes are modified so that the in-plane orientation of fibres is minimised.[22] When producing paper-like foam-formed products, the water is removed by vacuum. The foam collapses and the fibres consolidate. After vacuum suction, the formed web is wet-pressed and the moisture left is removed by contact or non-contact drying methods. When producing bulky structures, the space occupied by the air bubbles is wanted to be left in the structure so mechanical pressure cannot be applied. The water is removed first by the influence of gravity and the rest of the water is removed by non-contact thermal drying. During the first stage, the water drains through plateau borders. Then the water is evaporated and finally the air bubbles rupture.[23,24] The challenge in the drying of thick foam-formed structures is the high initial moisture content which leads to long drying times. The objective is to minimise the drying time without losing the thickness.[24] Timofeev *et al.*[24] have

studied different non-contact drying methods for thick and porous foam-formed fibre mats. Oven drying, air impingement drying with vacuum, air impingement drying coupled with infrared radiation and through-air drying were tested. Drying temperatures of 90 °C and 150 °C were used. Increasing the temperature from 90 to 150 °C decreases the drying time significantly. The lowest shrinkage and the shortest drying time were achieved by the combined air impingement-infrared drying. Good quality was also maintained by oven drying, but the drying times were remarkably higher. When using oven drying at 90 °C, the total drying time was 250 min whereas by the combined impingement-infrared drying the total drying time was only 40 min. The results also showed that fibre foam mat becomes air-flow-permeable at an average moisture content of 2-3 kg/kg. It was concluded that through-air drying could be applied as the final drying stage to speed up drying without losing thickness.

There is an increasing interest to replace non-renewable fossil fuel-based raw materials with biodegradable materials e.g. in packaging, composites and construction materials.[24,25] Conventionally used thermal insulation materials include glass and rock wool and different synthetic polymer materials. Cellulose-based insulation materials have been long on the market, but they have not received great popularity because they possess poorer thermal insulation properties compared to other materials. Bulky and highly porous foam-formed structures made from natural fibres show a potential to be used as thermal insulation or sound absorption materials.[23]

Pöhler *et al.*[23] have compared thermal insulation properties and strength properties of foam-formed fibre panels made from softwood, hardwood and thermomechanical pulps with three commercial thermal insulation materials. Two of the commercial products were glass wool and one was a cellulose wadding product composed of recycled newsprint, recycled cotton fibres and thermofusible textile fibres. Bulk densities of the foam-formed fibre panels were between 23-88 kg/m^3. Glass wool products had bulk densities of 29 and 18 kg/m^3 and the cellulose wadding product 42 kg/m^3, respectively. Thermal insulation properties of the foam-formed fibre panels were better than those of the cellulose wadding product, as the foam-formed materials had lower thermal conductivities and higher air flow resistivity. The foam-formed materials did not achieve as low thermal conductivity values as glass wool products at the same bulk density level. However, when bulk density increased to 45 kg/m^3, thermal conductivities of foam-formed materials decreased and a thermal conductivity level similar to glass wool could be achieved. Pulp type had a clear effect on the air resistivity and strength properties. From the foam-formed materials used, thermomechanical pulp (TMP) showed the best properties to be used as thermal insulation material. Fibre panels made of TMP had excellent

compression strength and bending stiffness compared to commercial products indicating that TMP could be used to make self-supporting insulation materials. It was also demonstrated that by foam forming versatile raw materials can be used. For example, glass fibres, synthetic fibres or mineral particles can be added to the papermaking pulp.

4 DETERMINATION OF SURFACTANTS

As anionic and non-ionic surfactant are the most widely used surfactants, this section is focused on the analysis of them. Figure 11 shows the most studied determination methods during the two last decades. Chromatographic and potentiometric techniques have been the most popular in recent years.[26] Spectrophotometric methods are still widely used due to their quickness and simplicity but they require the use of organic solvents which results in toxic wastes.[7]

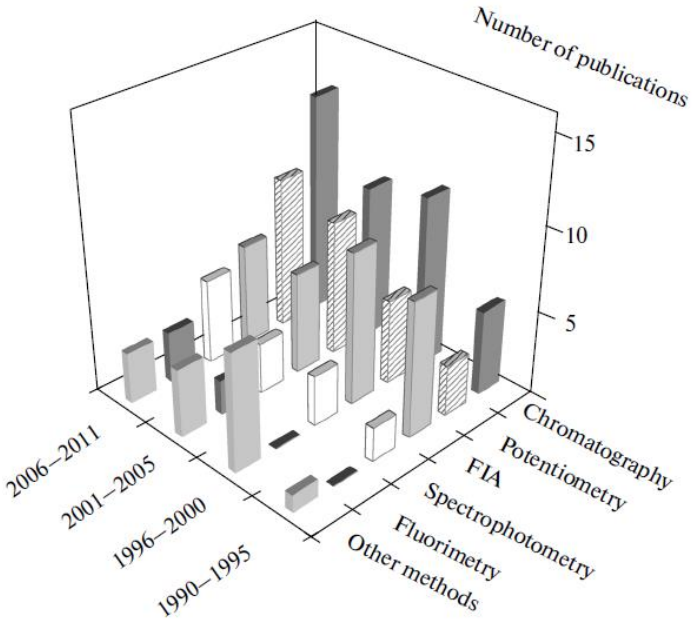


Figure 11. The distribution of the research on different determination methods of anionic surfactants. Reprinted with permission from[26]. Copyright (2014) Springer Nature.

4.1 Sample pre-treatment

When the sample matrix is complicated and surfactants exist at trace levels, it is necessary to pay attention to sampling and isolation of an analyte. To prevent biodegradation of surfactants,

environmental water samples are preserved by the addition of biocides, filtering and refrigeration. The general approach is to add formaldehyde and preserve the sample in the refrigerator at 4 °C. Still, water samples should be analysed within 48 h to prevent biodegradation. Solid environmental samples are freeze-dried, grinded and stored at 4 to 20 °C.[3,7]

4.1.1 Extraction of surfactants from solid sample matrices

For solid samples, e.g. soils, sediments and sewage sludges, the sample preparation is often the critical part of the analysis as the analytes must be transferred into a liquid phase in order to analyse them. Sample preparation may include many steps. First, the analyte is isolated from the solid sample by extraction. After extraction further purification steps may be needed to exclude other compounds, e.g. filtering, liquid-liquid extraction and solid phase extraction. In environmental samples, surfactants often exist at trace levels so the extracts must be pre-concentrated to achieve measurable concentrations.[3,27] There exist several methods of solid-liquid extraction. Conventional methods are Soxhlet and ultrasound-assisted extraction. Novel methods of solid-liquid extraction include microwave-assisted extraction (MAE), pressurised liquid extraction (PLE) and supercritical fluid extraction (SFE). Methanol is commonly used extraction solvent for surfactants, but also hexane, dichloromethane and acetone have been used for more hydrophobic surfactants.[7]

Soxhlet extraction has been the primary method of solid-liquid extraction for over a century. Soxhlet extraction is based on a continuous flow of solvent through the sample. In the conventional method, the sample is placed in a cellulose thimble-holder inside a refluxing apparatus (Figure 12a). The extraction cycle begins, when the solvent evaporates from a distillation flask. The solvent is condensed and collected into the extractor. The thimble-holder is gradually filled with the solvent and when the over-flow level is reached, the solution carrying the extract within flows back into the distillation flask. The solvent is then evaporated again and the new extraction cycle begins.[27] The analyte is transferred effectively into the liquid, because the solid sample comes into contact with fresh solvent repeatedly. Due to the cellulose thimble-holder, filtering is not needed after the extraction. The conventional Soxhlet extractor is also cheap, easy to use and the extraction can be modified easily. However, the conventional method requires long extraction time and the use of high amounts of organic solvents, often also toxic ones. Therefore, several modifications to the conventional Soxhlet extractions have

been made aiming at shortening the extraction time, decreasing the solvent usage and automation of the extraction process.[27]

Commercial automated versions of Soxhlet extractor are usually known as Soxtec devices (Figure 12b). In Soxtec, reflux boiling is combined with extraction and the extraction includes repeated boiling and rinsing steps.[27] Extraction time is 45 min whereas in the conventional Soxhlet extraction, extraction times of 4-18 hours have been used for extracting surfactant.[7] Also the consumption of the solvent is reduced to 50-100 ml and the solvent is partially recovered which reduces the amount of waste.[7,27] Soxhlet extraction has been enhanced by the use of ultrasound, microwave irradiation and high pressure. The most used commercially available microwave-assisted Soxhlet extractor is Soxwave-100 by Prolabo. By the use of ultrasound and microwaves more energy is gained to break the interactions between the analyte and the sample matrix.[27]

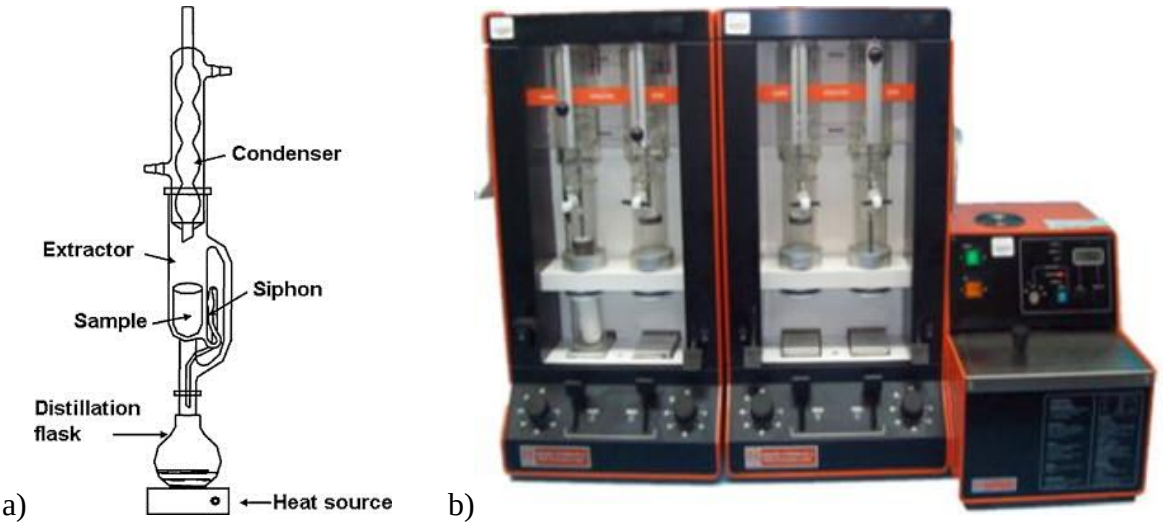


Figure 12. a) An illustration of the conventional Soxhlet extractor versus b) an automated Soxtec® System HT equipment with four extraction units. Reprinted with permission from[27]. Copyright (2010) Elsevier.

Ultrasound-assisted extraction is another simple and cheap technique that has been used successfully for the extraction of surfactants. Petrović and Barceló used ultrasound-assisted extraction for the determination of polyethoxylates, LAS and polar degradation products from sewage sludge. The freeze-dried and homogenised sample was sonicated 20 min in a solution of MeOH/CH_2Cl_2 (7:3, v/v). After sonication the mixture was centrifuged and the extract was collected. Sonication treatment was repeated three times. The obtained extract was pre-concentrated and further purified by solid-phase extraction. The recovery rates ranged from 84 to nearly 100 %.[28]

Above-mentioned extraction methods usually require large volumes of organic solvents. New extraction techniques for solid sample matrices have been developed in order to reduce solvent consumption and extraction time: microwave-assisted extraction (MAE), pressurised liquid extraction (PLE) and supercritical fluid extraction (SFE).[7] In microwave-assisted extraction, the sample is placed in a closed vessel with the extraction solvent and irradiated in a microwave oven when the temperature rises above 100 °C.[7,29] MAE can be applied for anionic and non-ionic surfactants. In pressurised liquid extraction, the extraction is performed in a high temperature and pressure so that the solvent does not boil. The sample is placed in a steel cell which has pores in the end caps so the solvent can flow through the cell. Temperatures from 75 to 150 °C are used and normally the pressure is kept at 1500 psi (10,4 MPa). Extraction at high temperature is more efficient because the solvent is more viscous and can penetrate through the sample better.[30] However, volatilisation of the analyte can restrict the choice of temperature. Usually temperatures of 100 and 120 °C have been used for extraction of surfactants.[7]

Supercritical fluid extraction is a relatively new technique as the potential of the technique was started to study around 1960. The possibility to replace organic extraction solvent has raised an interest especially to industrial applications.[31] The supercritical fluid can be considered as one state of matter. A compound is in a supercritical state if the temperature and pressure are above the critical values (T_c and p_c). In the supercritical state, the viscosity of gas state can be achieved but due to high pressure, the density remains as high as for liquids. Also the diffusivity is much higher than in liquid state.[32] Carbon dioxide is the most used supercritical solvent but many surfactants, for example LAS, have low solubility in CO_2.[3,31] For extraction of surfactants, methanol is often added to the CO_2 to improve extraction. Although, this usually results in lower selectivity because other compounds are extracted as well. The advantages of SFE are the low consumption of organic solvents, the easy removal of extractant and the possibility to fine-tune solvent properties by changing the pressure.[3] There are fewer studies dealing with the use of SFE for extracting surfactants due to the development and automation of other solid-liquid extraction techniques.[7]

4.1.2 Purification and pre-concentration

Before the analysis of surfactants, aqueous samples or extracts from solid samples need to be purified and pre-concentrated. Traditional liquid-liquid extraction (LLE) made in a separatory funnel is a versatile method for extraction of surfactants from water samples. Liquid-liquid extraction is performed using two immiscible or partially miscible liquids. When the two liquids

are mixed in a separatory funnel, the compounds are distributed between the two liquids according to their relative solubility. Usually the surfactant is transferred from an aqueous solution to an organic solution, but sometimes organic impurities are extracted in the organic phase while the surfactant remains in the aqueous solution.

Often the challenge in LLE of surfactants is emulsion formation. If an emulsion is formed, methanol or ethanol can be added until the emulsion is broken down. Emulsion formation can also be inhibited by increasing the ionic strength of the aqueous solution by adding e.g. sodium chloride or sodium sulphate. The greater the amount of surfactant to be extracted, the more easily the emulsion is formed.[3]

Ion pair formation is utilised in LLE of ionic surfactants. An ionic surfactant that is usually insoluble in chloroform or methylene chloride, can be extracted from a water solution by forming an ion pair e.g. with an ionic surfactant having opposite charge. This property is utilised e.g. in solvent extraction spectrophotometry and two-phase titration methods. Single LLE procedure is often difficult to apply, especially for simultaneous extraction of different surfactants, because the hydrophilicity of surfactants differs. Even for a single surfactant, LLE can be challenging because commercial surfactants are impure having a distribution of different chain lengths and ethoxylated parts.[3]

For LLE of anionic and cationic surfactants from water samples, chloroform with an ion pair reagent is the most widely used.[7] For LLE of non-ionic surfactants from water samples, e.g. dichloromethane, ethyl acetate and toluene are used.[3,7] The LLE procedure depends on the sample matrix and impurities to be separated from surfactants. Oils or organic impurities are often extracted from a mixture of an alcohol and water in a nonpolar solvent, e.g. in pentane. Inorganic salts are separated from surfactants in aqueous solution with high ionic strength.[3]

Solvent sublation is one of the adsorptive bubble separation techniques, which also include foam fractionation and flotation techniques.[33] Solvent sublation was a popular separation and pre-concentration method for surfactants a few decades ago. In solvent sublation, an inert gas (usually nitrogen) is passed through an aqueous sample. Surfactants adsorb on the surface of gas bubbles and are transferred within the bubbles to the upper water-immiscible organic phase. Figure 13 presents an illustration of solvent sublation apparatus. The ionic strength of the aqueous solution must be high. Commonly, ethyl acetate has been used as the organic solvent.[3] Solvent sublation is very similar to LLE, both are based on transferring the analyte from a water solution to a water-immiscible solvent, but in solvent sublation, the two phases are not in equilibrium. The transfer of surfactant is not limited by an equilibrium constant, so more analyte

is transferred into the organic solvent from the aqueous phase.[3,34] For high molecular weight non-ionic surfactants the recovery rates are low.[3] If there are solid particles present in the sample, sublation must be performed several times because some of the surfactant is adsorbed on the surface of particles.[35]

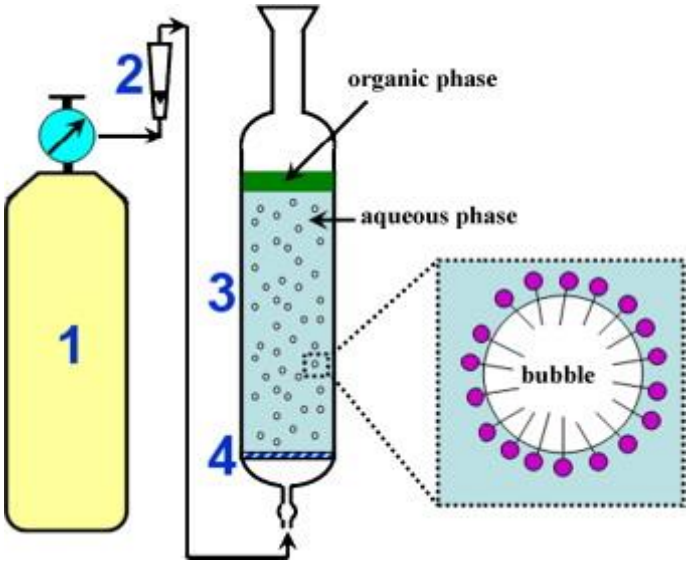


Figure 13. Solvent sublation apparatus: 1) Nitrogen cylinder, 2) rotameter, 3) flotation cell, 4) sintered glass disk with G_4 porosity. Reprinted with permission from[34]. Copyright (2010) Elsevier.

Solid phase extraction (SPE) is the most widely used purification and pre-concentration method in determination of surfactants. Compared to LLE, SPE is faster and requires less sample and solvent. The sample volume needed is 7-100 ml and the solvent volume is 5-20 ml.[7] SPE is based on the partitioning of the analyte between a liquid and solid sorbent. The target analyte interacts with the solid sorbent and is retained, while other compounds are excluded. Generally, SPE includes four stages that are represented in Figure 14. Firstly, the solid sorbent is conditioned so that it can interact with the target analyte. Then the sample solution is run through the sorbent. At this stage, the analyte and some impurities are retained by the sorbent while most of the impurities are extracted away. After sample addition, the sorbent is washed using a washing solution that releases only the remaining impurities while the analyte is still bonded to the sorbent. At the elution stage, the target analyte is released from the sorbent. This requires that the analyte interacts more strongly with the elution solvent than with the sorbent. Low volumes of elution solvents are used so that a concentrated sample is gained.[36]

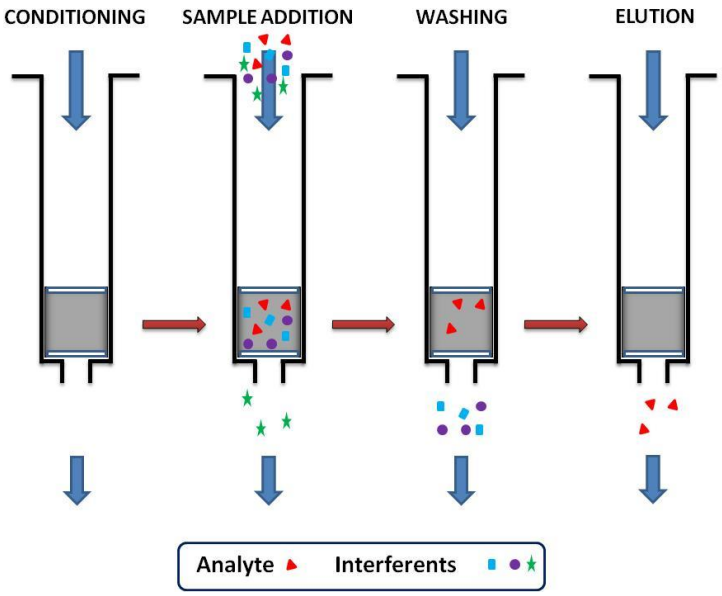


Figure 14. The phases in solid phase extraction procedure.

There are off-line and on-line SPE procedures. Off-line SPE is a part of the sample preparation process whereas in the on-line procedure, SPE is connected to high-performance liquid chromatography or gas chromatography system. There are several different formats of SPE. The most popular format is the cartridge inside a syringe barrel. The cartridge consists of two frits, the bottom frit containing the sorbent material. The frits are porous materials generally made of polyethylene, stainless steel, and Teflon. Extraction disks are also used widely. Higher flow rates can be used with extraction disks than with cartridges, which is beneficial when concentrating the sample.[37]

The choice of the sorbent material affects strongly on the selectivity and the yield of SPE. The analyte can interact with the sorbent e.g. via hydrophobic interactions, hydrogen bonding, dipole-dipole interactions, electrostatic interactions or π-π-interactions. Traditionally sorbents can be classified into normal phase, reversed-phase and ion exchange sorbents. In normal phase conditions, the sorbent surface is polar so it is suitable for retaining polar compounds from nonpolar media. In reversed-phase conditions, the sorbent is nonpolar retaining the analyte through hydrophobic interactions and a nonpolar solvent is needed to elute the analyte. Reversed-phase conditions are used to retain nonpolar compounds from aqueous media. Ion exchange sorbents retain only charged compounds and non-ionic compounds are excluded.[36,37]

Often the sorbents are either silica-based or polymer-based materials. Unmodified sorbent materials include silica, magnesium silicate and alumina, which are polar sorbents. Pure silica is a highly polar sorbent, which is not suitable for retention of less polar compounds. The polarity of the silica-based sorbent can be modified by bonding functional groups on the surface

of silica. For normal phase conditions, silica is modified with cyano, diol or amino groups, which make the sorbent less retentive toward highly polar compounds. Introducing alkyl or aryl groups, e.g. C_2, C_8 or C_{18} alkyl chains, cyano and phenyl groups makes the sorbent nonpolar and suitable for reversed phase conditions. The most widely used polymer sorbent material is styrene-divinylbenzene copolymer (PS-DVB), which is a hydrophobic material. The advantage of PS-DVB is stability over the whole pH range.[36,37] A new hydrophilic-lipophilic copolymer of *N*-vinylpyrrolidone and divinylbenzene for SPE have recently been invented (Oasis® HLB) and it has been applied for extraction of surfactants.[7,37] Ion exchange sorbents contain charged groups bonded to silica. Retention happens only in pH area in which both the sorbent and the analyte are charged. The analyte is eluted when either of the charged groups is neutralised. This is enabled by adjusting the pH of the elution solution. In cation exchange sorbents, silica is modified either with aliphatic sulphonic acid or with aliphatic carboxylic acid. The sulphonic acid is highly acidic and is negatively charged at all pH levels, which makes it a strong cation exchanger (SCX) whereas carboxylic acid groups are weak cation exchangers (WCX). Respectively, anion exchange sorbents contain either aliphatic quaternary amines (SAX) or aliphatic aminopropyl groups (WAX).[36]

For SPE of anionic and non-ionic surfactants, octadecyl silica (C_{18}) and graphitised black carbon (GBC) cartridges are the most widely used. C_{18} and GBC enable simultaneous extraction of anionic and non-ionic surfactants and their degradation products. Separation of different surfactants can be performed by fractional elution. Strong anionic-exchange resins have also been used e.g. for linear alkylbenzene sulphonates. For anionic surfactants, methanol is the most common elution solvent while for non-ionics also e.g. dichloromethane, ethyl acetate, acetonitrile and various solvent mixtures are used. Non-ionic surfactants can be separated from cationic and anionic impurities using SCX and SAX cartridges as they retain the ionic compounds but the non-ionic surfactants go through. SPE of cationic surfactants (e.g. QACs) using nonpolar silica sorbents is not possible, because the silanol groups of silica interact strongly with the cationic surfactants resulting in poor elution. Effective SPE of cationic surfactants can be achieved using alumina or anion exchange resins with SDS. SDS forms hemimicelles on the surface of the sorbent and cationic surfactants are electrostatically bonded.[7] P. Bassarab *et al*.[38] developed a SPE procedure for extraction of QACs from seawater using a neutral polymeric sorbent (Strata-X). They found that cationic surfactants adsorbed in the surface of the glassware resulting in significant recovery loss. Recoveries of 90-130 % were achieved by pre-saturating the glassware with a strong quaternary ammonium surfactant solution.

4.2 Spectrophotometric methods

4.2.1 UV absorption

Direct determination of surfactants by UV absorption can be applied for surfactants having aromatic groups in their structure. The method is very simple and cheap, as it does not require the use of organic solvents. The surfactant concentration can be measured directly from a water solution. The wavelength having the greatest absorptivity is chosen by scanning the wavelengths and the absorbance of the sample is measured in a quartz cuvette. For example, LAS, alkylphenol ethoxylates and imidazoline surfactants can be determined by UV absorption. LAS have absorbance maximums at around 193 and 223 nm, alkylphenol ethoxylates at around 223 and 276 nm, and imidazoline surfactants at around 235 nm. However, the method is susceptible to interferences because many other organic compounds also absorb at the UV region. The method is suitable for relatively pure sample matrices.[3]

4.2.2 Solvent extraction spectrophotometry

Solvent extraction spectrophotometric techniques are more popular than a determination by direct UV absorption. Solvent extraction spectrophotometry is based on the formation of a coloured ion pair that can be detected spectrophotometrically in the visible light area. The ion pair is soluble in organic solvents whereas the dye or the surfactant is not. The ion pair is extracted into an organic phase, and the surfactant concentration can be determined spectrophotometrically, as it is proportional to the colour change of the organic phase. Often used organic solvents include chloroform, dichloromethane and toluene. Anionic surfactants form ion pairs with cationic dyes and cationic surfactants with anionic dyes. Non-ionic surfactants form an extractable ion associate together with large cations (usually ammonium, potassium or barium) and anionic dyes. The EO units interact with cations and positively charged complex interacts electrostatically with the anionic dye. Usually, in solvent extraction spectrophotometric techniques, pH must be adjusted to an area where the complex formation is possible, i.e. both the dye and the surfactant are charged.[3]

Solvent extraction spectrophotometry is suitable for the determination of total anionic, cationic or non-ionic surfactant concentration. If an individual surfactant is wanted to quantify from a surfactant mixture, extractions or other separation techniques to isolate the analyte must be performed. Compared to direct UV absorption, lower concentrations can be detected by solvent extraction spectrophotometry. However, methods utilising ion pair formation are also susceptible to interferences. If there are other ionic compounds in the sample matrix that are

capable of forming a complex with the dye, the results are higher. Conversely, other ionic material that can form a colourless ion pair with the surfactant, give lower results.[3]

For the determination of anionic surfactants, many cationic dyes have been applied, methylene blue being the most widely used. Others include e.g. acridine orange, neutral red, dimidium bromide, methyl green and ethyl violet. Structures for the cationic dyes are presented in Figure 15.[3] With dimidium bromide and ethyl violet, greater sensitivity has been achieved compared to methylene blue method. The ion pair of ethyl violet and an anionic surfactant is more completely transferred into the organic phase allowing determination of trace amounts of surfactant with higher sensitivity. Chloride and nitrate are common interfering substances that form extractable complexes with cationic dyes. These interferences are eliminated by washing the organic phase with water or matching the interfering substance content of the blank to the same level.[3,39]

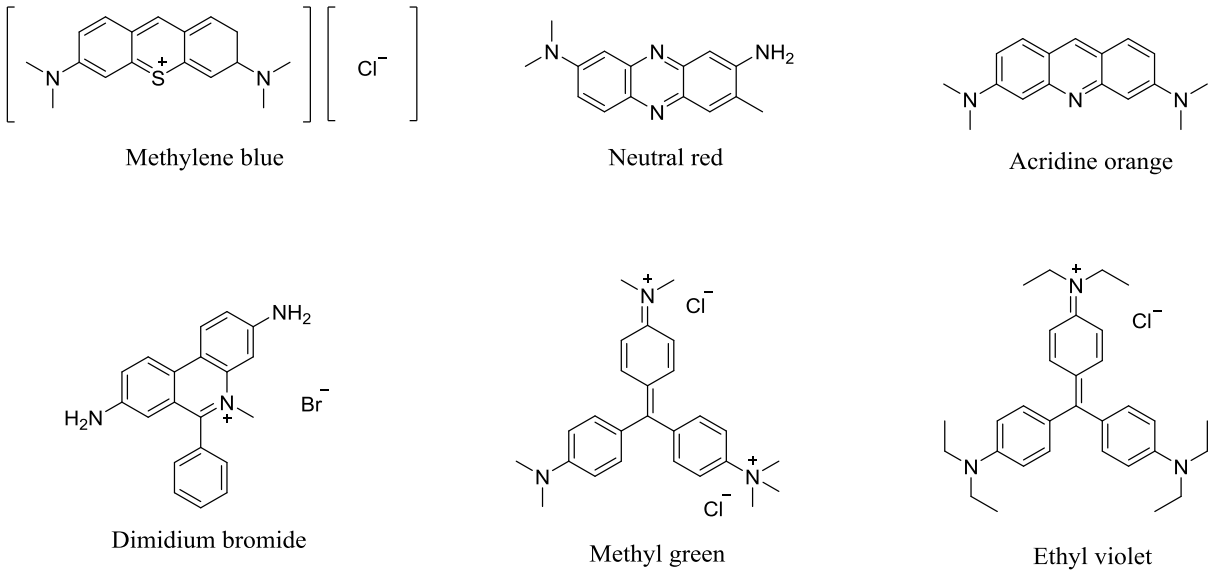


Figure 15. Examples of cationic dyes used in solvent extraction spectrophotometry.

Methylene blue method is the most frequently used for the spectrophotometric determination of anionic surfactants. Scheme of one standard procedure is presented in Figure 16. In that procedure, neutral MB solution and disodium phosphate buffer solution are added to 100 ml of water sample that contains up to 0.5 mg/l of surfactant. The sample is extracted three times with chloroform. The $CHCl_3$ phases are collected and combined after which water and acidic MB solution are added and one more extraction is performed. The obtained extract is diluted to 50 ml volume and the absorbance is measured at 650 nm. Although, the wavelength can vary slightly depending on the surfactants. There also exists a standard where Na_2HPO_4 solution is used for washing the extracts. This step raises the final $CHCl_3$ volume to 100 ml.[3,40]

Because the standard method is time-consuming and requires large volumes of sample and chloroform, several modifications have been developed. Jurado *et. al.* have been used a simplified method where the ion-pair formation reaction, extraction and absorbance measurement are all made in a 10 ml glass tube. In the method, 5 ml of sample, 200 µl of sodium tetraborate buffer, 100 µl of acidic MB solution and 4 ml of chloroform are combined and the mixture is stirred for 1 min. The phases are allowed to separate for 5 min after which the surfactant concentration can be measured. The simplified method can be applied to water samples that are relatively clean i.e. interfering substances do not exist.[40]

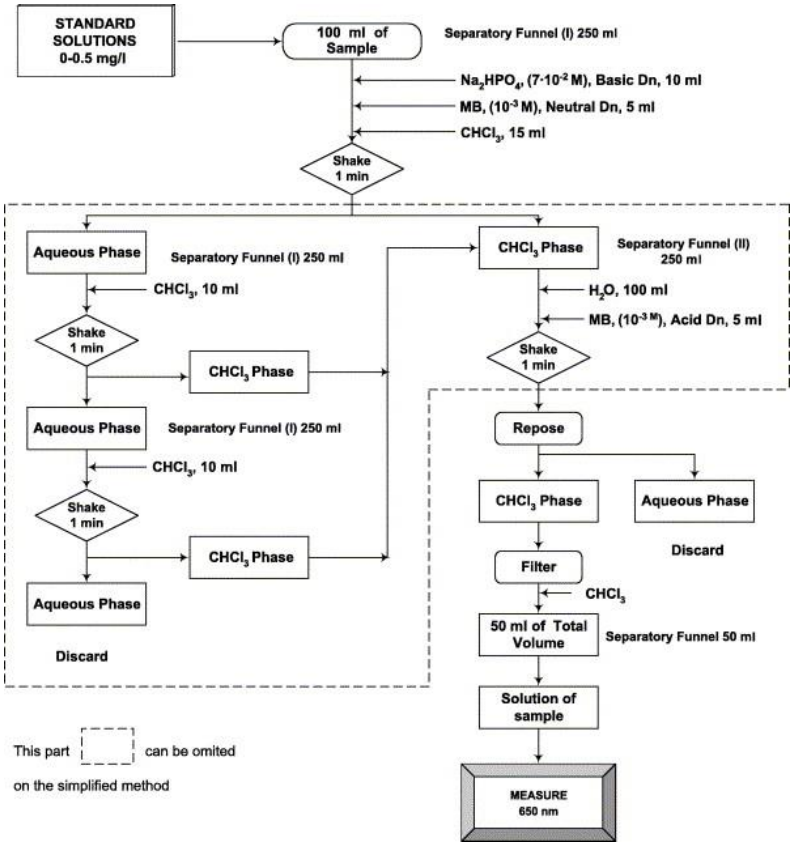
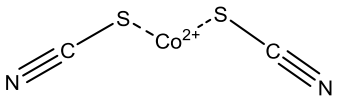


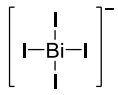
Figure 16. Scheme of the analytical procedure of the standard methylene blue method and the simplified method. Reprinted with permission from[40]. Copyright (2006) Elsevier.

Some anionic dyes used for the determination of non-ionic surfactants are presented in Figure 17. Among the spectrophotometric determination methods for non-ionic surfactants, the cobalt thiocyanate method is the most widely used. Ammonium cobalt thiocyanate reagent is used to form the complex, which is extracted in dichloromethane. The absorbance is usually measured at 620 nm. The method can be applied to non-ionic surfactants that have more than four moles of ethylene oxide units in their structure. Complexation with potassium picrate gives much higher sensitivity compared to the cobalt thiocyanate method, but it is less frequently used because picric acid is an explosive. Non-ionic surfactants can also be determined indirectly by

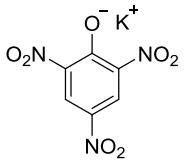
Dragendorff method in which non-ionic surfactants are precipitated by barium tetraiodobismuthate. The precipitate is collected and dissolved in ammoniumtartrate solution after which the amount of bismuth ion is determined spectrophotometrically by forming EDTA complex. Usually halogenated solvents are used in the solvent extraction spectrophotometric techniques for non-ionic surfactants.[3]



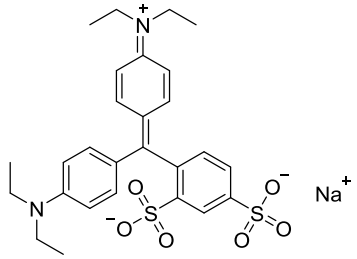
Cobalt thiocyanate



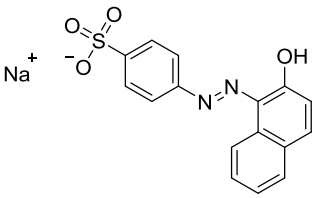
Tetraiodobismuthate



Potassium picrate



Disulfine blue VN



Orange II

Figure 17. Examples of anionic dyes used in solvent extraction spectrophotometry.

The disadvantage of spectrophotometric determination methods for non-ionic surfactants is the difficulty of calibration. The amount of EO units affect the absorptivity. Usually the calibration is made using a single type of surfactant, and the distribution of EO chains is known. However, in the samples the distribution can be different, especially when analysing mixtures of non-ionic surfactants. Hence, solvent extraction spectrophotometry is best suited for determination of a specific non-ionic surfactant rather than a determination of the total non-ionic surfactant content.[3]

Same anionic dyes as for non-ionic surfactants are also used for the spectrophotometric determination of cationic and zwitterionic surfactants. Therefore, non-ionic surfactants cause positive interference in the presence of large cations. The disulphine blue method is the most frequently used. However, the complex formation with disulphine is easily affected by changes in pH and mixing. Orange II has also been used as an ion pair reagent for cationic surfactants. It is more selective than other methods. By adjusting the pH to neutral, QACs can be selectively determined. At low pH, tertiary amines and zwitterionics can be determined.[3]

4.3 Chromatographic methods

The main advantage of chromatographic techniques over spectrophotometric and titrimetric techniques is the ability to separate and quantify individual surfactants. This is particularly important when analysing surfactants in environmental samples.[3,7]

4.3.1 General about chromatography

In chromatography, the separation of compounds is based on different partitioning between a mobile phase and a stationary phase. The sample is carried by a mobile phase through a column. The mobile phase is either a liquid or a gas. The stationary phase is inside the column and it is typically a viscous liquid coated to the solid surface of an open tubular column or composed of solid particles in a packed column. The mobile phase moves in a column at a constant velocity and compounds in the sample are partitioned between the mobile and the stationary phase. The stronger the interactions between the compound and the stationary phase, the longer it is retained in the stationary phase i.e. the longer it gets to travel through the column.[41,42] Chromatographic methods can be divided into following types based on the type of interaction with the stationary phase: adsorption chromatography, partition chromatography, ion-exchange chromatography, molecular exclusion chromatography and affinity chromatography.[41]

The total time it takes for a compound to travel from the one end to the other end of the column is called the retention time,

$$t_\mathrm{r} = t_\mathrm{s} + t_\mathrm{m}, \tag{3}$$

where t_r is the retention time, t_s is the time spent in the stationary phase and t_m is the time spent in the mobile phase. However, as the retention time depends also on several other thing, e.g. the column length, the retention of the compound is often described by the retention factor *k*, which is a dimensionless quantity.

$$k = \frac{t_\mathrm{r} - t_\mathrm{m}}{t_\mathrm{m}} \tag{4}$$

The retention time of a compound depends only on the time the compound spends in the stationary phase, as all the compounds in the sample spend the same amount of time in the mobile phase. To separate compounds, their retention times must be different.[42]

The compound is detected at the end of the column. The detected compounds are presented in a chromatogram, which is a plot of signal versus time. Ideally, the analytes form symmetrical

Gaussian type peaks in the chromatogram. The analyte concentration is proportional to the peak area. For a precise quantification, the peaks must not overlap. Separation factor is an important parameter that describes how well two compounds are separated from each other i.e. the resolution.

$$\alpha = \frac{k_B}{k_A}, \tag{5}$$

where k_B is the retention factor of the compound B and k_A is the retention factor of the compound A. The compound B is eluted after compound A, so B has a higher retention factor.[42]

The column's ability to separate compounds is described by the number of theoretical plates

$$N = \left(\frac{t_\mathrm{r}}{\sigma}\right)^2 = 5.54\left(\frac{t_\mathrm{r}}{W_{1/2}}\right)^2, \tag{6}$$

where N is the plate number, t_r is the retention time and $W_{1/2}$ is the peak width at half maximum height. A column having a high plate number is able to produce narrow peaks i.e. better resolution. The plate number is proportional to the length of the column. Longer columns have higher plate numbers and are able to produce better separation. In order to compare columns with different lengths, plate height H is used

$$H = \frac{L}{N}, \tag{7}$$

where L is the length of the column. The smaller the plate height, the narrower peaks are produced.[42]

Retention factor k, separation factor α and the number of theoretical plates N are combined in the general resolution equation

$$R = \frac{\sqrt{N}}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k_\mathrm{B}}{1 + k_\mathrm{ave}}\right) \tag{8}$$

where k_B is the retention factor of the compound of interest and k_ave is the average retention factor for the two compounds whose separation is studied.[42]

However, peak broadening depends also on diffusion and other physical processes that affect on the movement of molecules. Diffusion means the random movement of molecules from a region of high concentration toward a region of low concentration as time passes. In the column, compounds experience radial and longitudinal diffusion. Generally, small molecules diffuse

more rapidly than large molecules. Compounds moving in the centre of the column do not interact with stationary phase whereas compounds moving near the stationary phase are occasionally retained in the stationary phase, which causes them to lag behind. Radial diffusion results in molecules movement from the centre of the column toward the stationary and vice versa. Thus, radial diffusion averages the time molecules spend in the stationary phase and reduces band broadening. In the beginning, compounds are moving as narrow bands in the column. The more time the compounds travel in the column, the more they diffuse in the longitudinal direction of the column leading to band broadening. Other processes that effect on band broadening are the existence of multiple paths and the mass transfer between the stationary phase and the mobile phase.[42]

4.3.2 High-performance liquid chromatography

High-Performance Liquid Chromatography (HPLC) is the most widely used technique for the quantitative determination of surfactants in quality control of commercial formulations but also in environmental analysis.[7,43] The advantage of HPLC over GC is that usually there is no need for derivatisation which reduces the time consumed for sample preparation. Large surfactants that are not volatile enough for GC analysis can be analysed by HPLC.[7]

Most often, the separation of surfactants is achieved in reversed-phase conditions using C_8 or C_{18} columns. In reversed-phase conditions, surfactants are separated according to increasing hydrophobicity and usually surfactants are eluted in the order of increasing chain length.[3,7] Analysis of surfactants by HPLC is disrupted by the presence of micelles. To prevent the micelle formation, the percentage of organic solvent in the mobile phase is usually relatively high.[43] Methanol/water and acetonitrile/water are the most commonly employed mobile phases.[3,7,43] pH and ionic strength of the mobile phase are adjusted. For example, sodium perchlorate salt is added in the mobile phase when analysing anionic or zwitterionic surfactants.[43] Today, gradient elution is commonly used in HPLC, which means that the percentage of the organic solvent is changed during the run. A typical example is a linear change from 80:20 water/acetonitrile mixture to 20:80 water/acetonitrile mixture. The use of gradient elution reduces the retention time and enables separation of compounds having different polarities.[42]

Normal phase conditions are rarely used in the determination of individual surfactants but can be applied for the separation of ethoxylated non-ionic surfactants (having low molecular weight). In normal conditions, non-ionics are separated in the order of increasing ethylene oxide

content.[3,43] Normal phase chromatography can also be used for the determination of poorly water-soluble surfactants, e.g. QACs in fabric softeners.[43]

Many different HPLC detectors have been used in the determination of surfactants: UV, fluorescence, conductivity, refractive index (RI), evaporative light scattering (ELS) and mass detectors.[3] Conventional HPLC with direct UV absorbance or fluorescence detection can be used in the determination of LAS and APEs. Fluorescence detection provides better sensitivity compared to UV detection. By using wavelengths as low as 195 nm, UV detection can be also applied for the determination of surfactants, which do not contain aromatic groups. Another way is the indirect UV detection by derivatising the surfactant. RI detectors are practically applicable to any surfactant but are not commonly used due to their insensitivity (high quantitation limits) and incompatibility with gradient elution.[3] ELS detection is ideal for analytes, which have low volatility and lack strong UV chromophores. HPLC-ELS has been used in the determination of non-ionic surfactants, e.g. Tween 80 and alkyl polyglucosides.[3,44,45]Also size exclusion chromatography has been employed for some higher molecular weight non-ionic surfactants (e.g. Tween 80). In size exclusion chromatography, in contrast to the other chromatographic techniques, the surfactant must be present at concentrations above its CMC in the mobile phase.[3,44]

Limit of detection (LOD) depends largely on the detection method used. For the determination surfactants by HPLC-ELS, LODs from 1.25 to 13 mg/l have been reported.[8,44,45] For HPLC-MS devices, the LODs are in the ng/l range.[2,38]

Ion chromatography coupled with conductivity detection is often used for the determination of ionic surfactants.[3,43,46–48] Conventional ion chromatography, which uses ion-exchange columns, is rarely used due to the limited options in changing the separation conditions. However, it has the advantage that only ionic materials are retained. When using ion-exchange columns, surfactants are eluted in the order of decreasing alkyl chain length. Ion-pair chromatography (also called mobile-phase ion chromatography) is more often used. In this technique, ion chromatography equipment with suppressed conductivity detection is used but the separation is done in reversed-phase conditions.[3] Nonpolar polymeric or mixed mode columns have been used in the separation.[46,48] An ion-pairing reagent is added to the mobile phase to enhance the retention of surfactant. The ion-pairing reagent forms a neutral complex with the surfactant.[46] For the determination of anionic surfactants mobile phases containing 5 mM lithium hydroxide or ammonium hydroxide have been used.[46,47,49] Organic ion-pairing reagents, e.g. tetrabutyl

ammonium hydroxide, further increase the hydrophobicity and are therefore suitable for ionic analytes having low molecular mass.[47]

In conductivity detection, the conductivity of the eluent is measured between two electrodes. As a band of ionic analyte passes through, the conductivity changes. However, the conductivity of the mobile phase (i.e. the baseline conductivity) itself is high because it is usually high in ionic strength. Especially H^+ and OH^- increase the background conductivity. Before coming to the detector, the eluent passes through an ion suppressor, which transforms interfering ions to neutral species. Neutral species do not conduct electricity and thus the background conductivity is reduced. Ion suppression is based on ion exchange. When analysing anionic species, cations are exchanged to H^+ and when analysing cationic species, anions are exchanged to OH^-. H^+ and OH^- neutralise the interfering ions present (e.g. formation of H_2O).[42] Figure 18 shows an example of a chromatogram obtained from the separation of C10-C18 sodium alkyl sulphates using ion-pair chromatography with conductivity detection.

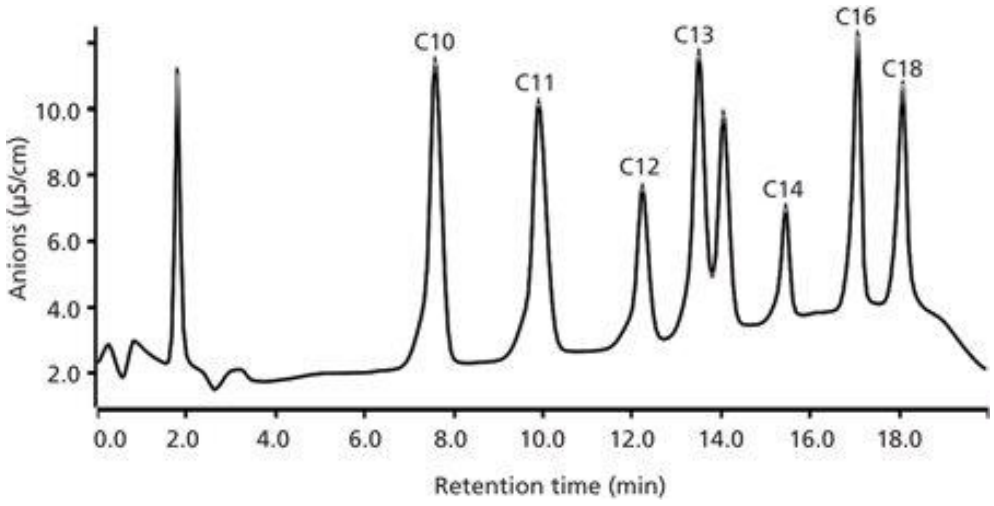


Figure 18. The separation of C10-C18 sodium alkyl sulphates using ion-pair chromatography with conductivity detection. The figure shows a chromatogram of 200 mg/l standard.[49]

Research has been carried out aiming at the determination of multiple surfactants in a single procedure. During the 2000s, HPLC coupled with mass spectrometry (MS) has been widely used for the determination surfactants.[2,8,28,50] This is mainly due to the development of ionisation techniques that can be coupled with HPLC. HPLC-MS offers many advantages: greater sensitivity and selectivity compared to other techniques, simultaneous determination of multiple analytes and the possibility to identify unknown surfactants and their degradation products.[2] HPLC-MS has become the most powerful technique for the determination of surfactants and their degradation products from environmental samples.[2,7]

In mass spectrometer, molecules are vaporised and ionised and the molecular ions are directed to the mass analyser where they are separated by electric or magnetic field according to their mass to charge ratio *m/z*. The chromatogram of LC/MS or GC/MS is typically a plot of total ion current versus time. The detection is based on compounds having specific *m/z* ratios. The mass spectrometer can also be operated in selected ion monitoring (SIM) mode, which means that the abundance of only a specific *m/z* ratio is detected. By choosing the *m/z* ratio characteristic to the compound of interest, the compound can be selectively analysed from a complex matrix. Because of the lack of overlapping peaks, lower LODs can be achieved in SIM mode. There are multiple ionisation techniques and mass analysers available.[42,51] Atmospheric pressure ionisation (APCI) and electrospray ionisation (ESI) are the ion sources that can be coupled with HPLC. Both ion sources contain a nebuliser that turns the eluent coming out from the column into fine spray. In ESI, the fine droplets are charged by passing through a semicylindrical electrode. The solvent is evaporated with the aid of nitrogen gas and eventually charged solutes are left in the gas phase. In APCI, the sample is turned into a gaseous state by heat after which the gas molecules are ionised by a corona discharge needle.[42] ESI and APCI ion sources can be used either in positive or negative ionisation mode which means that either positively or negatively charged molecular ions are produced, respectively.[28,52]

The most popular mass analysers include single quadrupole, triple quadrupole, ion trap and time-of-flight (ToF).[51] Quadrupole mass analyser is frequently used in surfactant analysis.[7] Triple quadrupole is an example of tandem mass spectrometry (MS/MS) in which multiple mass analysers are connected in series. The first mass analyser isolates a molecular ion with specific *m/z* ratio is selected. This so-called precursor ion is then subjected to fragmentation and the fragment ions are separated by the following mass analyser.[51] Sensitivity and selectivity are increased by tandem mass spectrometry because compounds have specific fragmentation patterns. This is useful especially in the analysis of environmental samples where interferences arise when different compounds show the same molecular ions.[7,42]

Anionic surfactants and polar degradation products of surfactants (e.g. sulphophenyl carboxylic acids, nonylphenol and nonylphenol ethoxycarboxylates) are analysed under negative ionisation mode. Cationic surfactants are analysed using positive ionisation mode. Due to the lack of charge, non-ionic surfactants are most commonly analysed in positive ionisation mode by forming cation adducts. The oxygen atoms of the polyethylene oxide chain interact with certain cations, e.g. sodium and ammonium, and allow the molecule to "wrap" itself around the cation. As a result, $[M+Na]^+$ or $[M+NH_4]^+$ molecular ions are detected. Sodium or ammonium can be added to the mobile phase, e.g. formic acid/ammonium formate buffer has been used.[2,7]

However, as the stability of the cation adducts of non-ionic surfactants is enhanced as the amount of EO units increases, the mass detector response greatly depends on the length of polyethylene oxide chain. Ethoxymers containing only one or two EO units have particularly poor stability.[2]

HPLC-ToF-MS is less commonly used than other HPLC-MS devices for the determination of surfactants.[2,7] Pablo A. Lara-Martín *et al*.[2] developed a method for the analysis of LAS, NPEO, AEO and their degradation products (SPC, NPEC and PEG) from aqueous and solid environmental samples by HPLC-ToF-MS. Due to the high sensitivity of ToF mass detector, very low LODs obtained. LODs for LAS were between 0.4-1.6 ng/l in water samples and between 0.9-8.9 µg/kg in marine sediment samples. LODs for NPEO and AEO were primarily below 1.0 ng/l in water samples between 0.1-4.0 µg/kg.

4.3.3 Gas chromatography

Gas chromatography (GC) is based on compounds' partitioning between a gas phase and a stationary phase. The carrier gas is an inert gas, usually N_2, H_2 or He.[42] Common stationary phase is a non-volatile liquid coated on the surface of an open tubular column i.e. a capillary, but also stationary phases composed of solid particles are used. The liquid stationary phase is chosen according to polarity. Nonpolar column for nonpolar analytes and polar columns for polar analytes. They are typically composed of a polysiloxane backbone and the polarity is adjusted by the attached groups, such as phenyl, methyl and nitrile groups.[41] The inner diameter of the capillary is 0.5 mm or less and the column length is typically 10-60 m. The thickness of the liquid coating is from 0.25 to 5 µm.[42]

The compounds analysed need to be in the gaseous state. Therefore, the sample is vaporised in an injector oven before entering into the column. The factors affecting the separation are the temperature, the carrier gas flow rate, and the type of the stationary phase. The analysis can be performed at a constant temperature (isothermal analysis) or by using temperature programming in which the temperature is increased by steps. Temperature programming is suitable for samples containing compounds that have different volatility. Typically, GC oven can be operated between 35 and 400 °C.[42]

GC enables complete separation of surfactant homologues and isomers. As the majority of surfactants are not volatile enough for direct determination, they need to be derivatised for determination by GC. Often used derivatising agents include e.g. *N*,*O*-

bis(trimethylsilyl)trifluoro acetamide (BSTFA), trifluoroethanol, acetic anhydride, diazomethane and hydrogen bromide.[7]

Several procedures have been applied in the determination of anionic surfactants to make the surfactant volatile including pyrolysis, chemical desulphonation and derivatisation. In pyrolysis, the surfactant is decomposed into linear alkanes and alkenes or other characteristic fragments in anaerobic conditions by heating to a high temperature (from 400 to 600 °C). Desulphonation is usually performed by reaction with phosphoric acid. Today, derivatisation is more commonly preferred. Sulphonate surfactants have been derivatised e.g. to sulphonyl chlorides, methyl sulphonates, trifluoroethyl sulphonates and methyl esters. In the analysis of alkyl sulphates and alkyl ether sulphates, often the susceptibility to hydrolysis is utilised. Acidic hydrolysis to form fatty alcohols or fatty alcohol ethoxylates is performed followed by analysis e.g. as trimethylsilyl or alkyliodide derivatives.[3] Direct derivatisation of alkyl sulphates can also be conducted if alkyl sulphate is converted to its hydrogen form. This can be done by passing alkyl sulphates through SCX column preconditioned with 0.1 M HCl.[3,53]

Gas chromatographic determination of non-ionic surfactants with a high degree of ethoxylation is challenging. Depending on the structure and the instrument characteristic, non-ionic surfactants containing up to 20 moles can be determined. Some low molecular mass AES, NP and short chain NPEOs have been analysed without derivatisation. Non-ionic surfactants have been analysed as trimethylsilyl and acetate ester derivatives. High molecular weight surfactants need to be cleaved into smaller fragments before analysis. In cleavage reactions, surfactants are generally cleaved between the hydrophobic and hydrophilic parts. Cleavage can be done with e.g. with hydrogen bromide, a mixture of acetic anhydride and *p*-toluenesulphonic acid or acetyl chloride with a ferric chloride catalyst. Reaction with HBr splits the polyoxyethylene surfactant into mono- and dibromoethane. Acetyl chloride cleaves the EO units producing 2-chloroacetate. By 2-chloroacetate, the amount of EO units can be quantitatively determined. If a surfactant structure includes fatty acid esters (e.g. sucrose fatty acid esters and ethoxylated sorbitan esters), the surfactant can be decomposed into the corresponding fatty acids by saponification. The fatty acids are then converted into methyl esters, from which the alkyl chain distribution can be easily analysed by GC.[3]

Traditionally, flame-ionisation detectors (FID) have been used in the determination of surfactants, especially for anionic surfactants.[3,7] FID has been the dominating gas chromatography detector for decades due to its sensitivity, low cost and simplicity.[54] In FID, the eluate coming out from the GC column is mixed with hydrogen gas and air and burned in a

flame tip. During the combustion, carbon atoms form CH radicals, which produce CHO^+ ions and free electrons with oxygen. There is an electric potential of 200-300 V between the flame tip and the collector electrode. Electrons are accelerated and move toward the collector-detector generating an electric current. The electric current is then converted to a voltage, amplified, filtered, and finally converted into a signal. Only about 1 of 10^5 carbon atoms undergoes the ionisation, but the amount of ions produced is directly proportional to the amount of compounds present. Lower detection limits are achieved when N_2 is used as a carrier gas. Therefore, often N_2 is added as "a makeup gas" to the eluate before the combustion.[41]

Nicholas J. Fendlinger *et al*.[53] have used GC-FID to the determination of different chain lengths of alkyl sulphates in river water and to monitor the removal of alkyl sulphates from municipal wastewaters. Alkyl sulphates were separated by SPE using C_2 RP and SAX columns followed by conversion to the hydrogen form by SCX. Alkyl sulphates were derivatised with N,O-bis(trimethylsilyl)trifluoroacetamide with 1 % trichloromethylsilane and analysed as trimethylsilyl ethers. Dimethylpolysiloxane capillary column was used in the analysis. It was discovered that the calibration could be done using the corresponding alcohols instead of alkyl sulphates which reduces the sample preparation steps. The detection limits for the determination of alkyl sulphates from river water and wastewater effluent was 5 µg/l and 10 µg/l from the influent.

Today, gas chromatography is more commonly coupled with mass spectrometry (MS) detector in the analysis of surfactants.[7] The most common modes of GC-MS are electron impact (EI) and chemical ionisation (CI). In EI ionisation, gaseous compounds are bombarded by a beam of accelerated electrons. The collisions lead to a formation of radical cations. In CI, the analytes collide with low molecular mass charged ions which are formed from the collisions between electrons neutral molecules (e.g. methane). This leads to the formation of protonated molecular fragments which are much more stable than radicals. EI-MS and CI-MS detectors are suitable for analysis of compounds having molecular mass < 1 000 Da.[51]

4.4 Atomic spectroscopy

Atomic spectroscopy techniques are typically used for analysis of inorganic materials so they have not been applied for surfactant analysis frequently.[3,55] Total concentration of anionic, cationic or non-ionic surfactants can be measured by atomic absorption spectroscopy (AAS) indirectly. The surfactant is extracted as an ion-pair into an organic solvent using an ion-pair reagent that contains an inorganic element that can be determined by AAS. For example

bis(ethylenediamine)copper(II) has been used for the determination of anionic surfactants, tetrathiocyanatocobalt(II) for cationics and potassium tetrathiocyanatozincate(II) for non-ionics.[3]

Akihiko Kawauchi[56] has used Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for the determination of LAS and alkyl sulphates from commercial laundry detergent products. The method is based on the direct determination from a water solution by measuring sulphur concentration. The surfactants are separated from inorganic sulphur by precipitation with calcium. LAS and alkyl sulphates can be determined separately by performing acidic hydrolysis before the precipitation. Alkyl sulphates are hydrolysed into alcohol and sulphate whereas LAS is not degraded. The described method showed similar results with traditional titration methods for LAS and alkyl sulphates.

4.4.1 General about ICP-OES

ICP-OES measures the amount of elements in liquid or gas samples based on atomic emission. In ICP-OES, the liquid sample is turned into a fine aerosol most commonly by a nebuliser in a spray chamber after which the sample is carried into a hot plasma by argon flow. In the plasma, the sample is atomised and even ionised when sufficient energy is available. The atoms and ions are excited and when the excitation state returns to the ground state, a photon is emitted. The amount of an element is measured by measuring the intensity of emission radiation at a characteristic wavelength. During the last few decades, ICP-OES has become a more popular device in analytics. In many applications, ICP-OES has replaced atomic absorption spectrometry (AAS). ICP-OES has a wide measuring range: from concentrations below 1 mg/l to hundreds of mg/l. Simultaneous determination of up to 70 elements is possible by ICP-OES. Due to a high atomisation temperature, fewer matrix interferences are observed. Also, the new techniques provide many tools to correct matrix interferences.[57]

Plasma is a medium that is composed of atoms, ions and free electrons. Inductively coupled plasma is generated from argon gas. The plasma is generated by electromagnetic induction in ICP “torch”. The torch is surrounded by load coil made from copper. When high-frequency electric current is applied to the load coil, it creates an oscillating magnetic field. A spark from a Tesla coil is used to initiate ionisation. The argon ions and free electrons are accelerated in the magnetic field. This is known as inductive coupling process. The argon ions and electrons collide with other argon atoms generating more ions and electrons. The plasma is seen within

the ICP torch as very bright and intense discharge.[57,58] Temperature of the plasma varies between 6 000-10 000 K depending on the zone.[58]

The sample is introduced into the plasma by the inner argon flow. Several different sample introduction systems have been developed, such as nebulisation, hydride generation, electrothermal vaporisation, and laser ablation. The different sample introduction systems differ e.g. in stability, cost, sample transport efficiency, susceptibility to clogging and compatibility with different sample matrix. Pneumatic nebulisers are the most popular sample introduction system. In pneumatic nebuliser, the aerosol is formed by high-speed argon flow. There are three different types of pneumatic nebulisers: the concentric nebuliser, the cross-flow nebuliser, and the Babington nebuliser.[57] Once the sample is introduced into the plasma, it undergoes desolvation, vaporisation, atomisation and finally, excitation and ionisation. The emission radiation is measured near the centre of the plasma. The temperature in the analytical zone of plasma is about 6 500 K.[58]

The emission can be observed in radial view, axial view or dual view mode. In the radial view, the emission is measured from the side of the plasma whereas in the axial view, the emission is measured from the end of the plasma. Dual view is a combination of the two configurations. In the radial view, the volume of the observed analytical zone is smaller, so there are fewer spectral and matrix interferences. The axial view provides better sensitivity, so lower limits of detection (LOD) can be achieved, but the disadvantage is that it is more susceptible to spectral and matrix interferences.[57]

The emitted light is separated into individual wavelengths in a monochromator or a polychromator. Due to the simultaneous determination of multiple elements, the density of the emission radiation is high and much higher resolution is needed in ICP-OES compared to AAS. Spectral bandpass of 0.01 nm or even lower is needed. Finally, the intensity of the characteristic emission lines are detected using a photomultiplier tube (PMT), a charge injection device (CID) or a charge coupled device (CCD).[57]

5 SURFACTANT RESIDUES IN THE PRODUCT

5.1 The chemical legislation, registration and authorities

5.1.1 Globally Harmonised System

Globally Harmonised System of classification and labelling of chemicals (GHS) is guidance developed by the United Nations aimed at using the same classification criteria and labels for hazardous chemicals around the world. Before GHS, label warnings and safety data sheets of hazardous chemicals differed between many countries. GHS protects users of chemicals and makes the international chemical trade easier. GHS is not legally binding so countries must adopt own regulations by GHS guidelines. GHS guidelines are given in the UN GHS Purple Book, which is updated every other year.[59] The latest revision (Rev. 7) has been given in 2017.[60] GHS serves so-called "building blocks" from which countries can choose the suitable ones for their needs. This means that GHS may not be fully adopted in every country, e.g. all the hazard classes in GHS may not be included. Many countries have implemented GHS, e.g. EU, USA, Canada, Brazil, China, Japan and Australia.[59] In the European Union, the principles of GHS are given in Regulation (EC) No 1272/2008, which is known as the Classification, Labelling and Packaging (CLP) Regulation.[61]

Chemicals are classified into hazard classes and hazard categories. Hazard class defines the nature of the hazard and the category how severe the hazard is. Hazard classes are divided into physical hazards, health hazards and environmental hazards. These include several subclasses. In the latest revision, altogether 29 hazard classes are defined. The hazard classes in which the chemical is classified determine signal words, hazard pictograms, hazard statements and precautionary statements that must be included in the product labelling and safety data sheets. GHS also determines the circumstances in which safety data sheets should be provided for a substance or mixture, the content of safety data sheets and the minimum information required. The hazard classes described in the latest UN GHS Purple Book and the hazard pictograms and their meanings are presented in Appendix 1.[59]

5.1.2 Chemical inventories

CAS REGISTRY[SM] maintained by Chemical Abstract Service is the largest chemical registry today. CAS Registry has become the international standard identification system for chemical substances and it is used by regulatory bodies. CAS Registry includes about 142 million chemical substances and the information is based on scientific literature. The database covers

the publications since 1907. Along with organic and inorganic compounds, the database also includes protein and DNA sequences. CAS number contains up to 10 digits.[62]

REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulation (EC) No 1907/2006[63] is the key element of European chemical legislation. According to REACH regulation, if a company manufactures or imports a chemical in amounts of 1 tonne or more per year inside EU member states or European Economic Area, the chemical needs to be registered. Only one registration for every chemical is made so companies manufacturing or importing the same substance, need to make the submission jointly. An important aim of REACH is the replacement of substances possessing high concern with less dangerous substances. In the registration dossier, the company/companies should prove that the chemical can be safely used and that the possible risks to human health or the environment are manageable. The intrinsic chemical, physical and toxicological properties of the chemical and information about the safe use, exposure and risk management are described. The registration dossier is submitted to the European Chemicals Agency (ECHA), which evaluates whether the risks are manageable and makes a decision about possible restrictions of use.

Before REACH came into force, there were three different chemical inventories, which were established by Directive 67/548/EEC on classification, packaging and labelling of dangerous substances and its amendments. EINECS (European Inventory of Existing Commercial chemical Substances) covers all substances "deemed to be on the European Community market between 1 January 1971 and 18 September 1981". ELINCS (European List of Notified Chemical Substances) lists so-called new substances that were placed on the market between 18 September 1981 and 31 May 2008. The definition of polymer was changed by the seventh amendment of Directive 67/548/EEC in 1992. NLP (List of No Longer Polymers) was established and it lists substances that were no longer considered as polymers. EINECS, ELINCS and NLP numbers consist of seven digits. Today, all the three inventories are under EC (European inventory) and EINECS, ELINCS and NLP numbers are now referred to as EC numbers. EC inventory consists of over 100 000 substances.[64] However, REACH regulation does not say anything about creating new EC numbers for substances that do not exist in EC inventory. Therefore, ECHA has been assigned list numbers for substances not belonging to EC inventory to ease the processing of submissions. The list numbers do not have any legal basis. EINECS, ELINCS, NLP and list numbers all are seven-digit numbers (xxx-xxx-x). EINECS numbers always start with 2 or 3, ELINCS number starts with 4 and NLP with 5. Numbers starting with 6, 7, 8 or 9 are list numbers.[65]

In the United States, there is a corresponding system, TSCA inventory. Section 5 of Toxic Substance Control Act requires to all chemicals manufactured or imported in the United States must be listed in TSCA inventory. If a company wants to manufacture or import chemical that is not listed in TSCA inventory, the chemical is considered as a "new chemical substance" and the company must submit Pre-manufacture Notice (PMN) to U.S. Environmental Protection Agency (EPA). PMN is reviewed by EPA within 90 days from the submission.[66] In the review process, EPA will assess the possible risks to human health and the environment. If the chemical is determined to "not likely to present an unreasonable risk", the company may start the manufacture or import. After the company has delivered a Notice of Commencement of Manufacture or Import (NOC), the chemical is added to the inventory and it becomes an "existing chemical". In addition, a significant new use notice (SNUN) for already existing chemical has to submitted if the chemical is considered to be used in a new way that may pose risks.[67]

5.2 Toxicity of chemicals

Chemical risk assessment includes toxicological and ecotoxicological studies, in which adverse effects of chemicals to living organisms are defined. In toxicology, the main subject is the effects of chemicals on humans whereas in ecotoxicology, the effects on other organisms are studied. Toxicological studies include e.g. acute toxicity, skin and eye irritation, sensitisation, repeated dose toxicity, mutagenicity and genotoxicity. In ecotoxicological studies, e.g. aquatic toxicity, bioaccumulation and biodegradability of chemicals are assessed.

In acute toxicity tests, the effects of single exposure or exposure within a short period are examined. Acute toxicity studies can be conducted through several different administration routes: intravenous, oral, dermal and inhalation. Acute toxicity is often described by LD_{50} or LC_{50} values. LD_{50} is the median lethal dose that causes the death of 50 % of the test population within a certain period (24, 48, 72 or 96 h). LC_{50} stands for the same phenomenon but it defines the median lethal concentration. These values are quite extreme measures. Usually the toxic effects observed in ecosystems are rather sublethal than lethal. The median effective concentration EC_{50} is the concentration that within a certain time period causes a specified adverse effect in 50 % of the population. The adverse effect can be e.g. 20 % reduction in growth. However, LD_{50} and LC_{50} do not tell much about the dose-effect relationship. Therefore, often a so-called threshold value is also determined. NOAEL (No Observed Adverse Effect Level) and NOAEC (No Observed Adverse Effect Concentration) values determine the greatest

dose and the greatest concentration, respectively, which do not cause severe alterations e.g. in function, growth or lifespan of an organism.

PBT and vPvB substances have very adverse effects on organisms. PBT stands for Persistent, Bio-accumulative and Toxic, and vPvB stands for very Persistent and very Bio-accumulative. For all the inherent properties (persistent, bio-accumulative, toxic, very bio-accumulative, very persistent), criteria have been set. A substance is considered as PBT or vPvB only if it meets the criteria for all the inherent properties. In EU, the criteria for PBT and vPvB substances are set in REACH regulation. Respectively, in the USA the criteria have been set by EPA under TSCA. The criteria in EU and USA are not the same. For example, according to the criteria in EU, a substance is considered to be toxic if the long-term NOAEC value for aquatic organisms is below 0.01 mg/l.[68]

5.2.1 Toxicological properties of surfactants

Due to the extensive use of surfactants in the household and industrial purposes, large amounts of surfactants are discharged in sewage treatment plants. In most sewage treatment plants, organic contaminants (such as surfactants) are removed from the wastewater by the combination of mechanical, chemical and biological treatment. The residual surfactants end up in the environment through effluent discharge in surface waters and sludge disposal on lands.[69] The environmental impact of surfactants is assessed e.g. by tests for aquatic toxicity, biodegradability and bioaccumulation.[6]

Surfactant classes can be roughly arranged in the order of decreasing toxicity according to the following: cationic, anionic, zwitterionic and non-ionic surfactants.[70] Because of their amphiphilic nature, surfactants are generally toxic to aquatic organisms. A surfactant is defined as toxic if the EC_{50}/LC_{50} is below 1 mg/l after 96 h testing on fish and algae and 48 h on daphnia. To consider as an environmentally benign surfactant, the values should be above 10 mg/l.[6]

For alkyl sulphates and alkyl ether sulphates EC_{50}/LC_{50} values are usually 1-100 mg/l whereas for LAS values below 1 mg/l have been reported. Table 5 shows LD_{50} and LC_{50} values for different anionic, cationic and non-ionic surfactants. None of the surfactants listed is considered as PBT or vPvB substance.

Table 5. Toxicity values for different anionic, cationic and non-ionic surfactants.

Surfactant name	Toxicity factor	Value	Ref.
SDS (for structure see Table 1)	LD_{50} oral (rat)[a]	977 mg/kg	[71]
	LC_{50} (fish)[b]	29 mg/l	
	EC_{50} (daphnia)[c]	6 mg/l	
Sodium dodecylbenzenesulphonate	LD_{50} oral (rat)[a]	500-2 000 mg/kg	[72]
	LC_{50} (fish)[d]	3.2-5.6 mg/l	
	EC_{50} (daphnia)[e]	6.3 mg/l	
Didecyldimethylammonium chloride (for structure see Table 2)	LD_{50} oral (rat)[a]	329 mg/kg	[73]
	LC_{50} (fish)[f]	0.19 mg/l	
	EC_{50} (daphnia)[c]	0.062 mg/l	
Triton® X-100 (for structure see Table 4)	LD_{50} oral (rat)	1 900-5 000 mg/kg	[74]
	LC_{50} (fish)[g]	0.26 mg/l	
	EC_{50} (daphnia)[c]	0.011 mg/l	
Tween® 20 (for structure see Table 4)	LD_{50} oral (rat)	38 900 mg/kg	[75]
	LC_{50} (fish)[h]	>100 mg/l	
	EC_{50} (daphnia)[c]	>10 mg/l	
Polyvinyl alcohol	LD_{50} oral (rat)[a]	>2000 mg/kg	[76]
	LC_{50} (fish)[h]	>5000 mg/l	
	EC_{50} (daphnia)[c]	8.3 mg/l	

a. OECD Test Guideline 401
b. Pimephales promelas (fathead minnow), 96 h test (OECD Test Guideline 203)
c. Daphnia magna (water flea), 48 h test
d. Oncorhynchus mykiss (rainbow trout), 96 h test (OECD Test Guideline 203)
e. Daphnia magna (water flea), 48 h test (OECD Test Guideline 202)
f. Pimephales promelas (fathead minnow), 96 h test
g. Leuciscus idus (Golden orfe), 96 h test (OECD Test Guideline 203)
h. Danio rerio (zebra fish), 96 h test (OECD Test Guideline 203)

There are a lot of data for aquatic toxicity of surfactants available. Variation exists in toxicity values for a given surfactant depending on the species tested but even within the same species tested. Therefore, predicted no effect concentration (PNEC) values have been calculated for surfactants. PNEC gives an estimation of the surfactant concentration that causes no effect in any aquatic species. PNEC values are derived from the existing toxicity data based on statistical calculation and compared with the no observed effect concentration (NOEC) values from laboratory or field studies. The calculation based on long-term toxicity data gives a more reliable estimate. According to the statistical method of Aldenberg and Slob, NOEC values from at least four different taxonomic groups should be used. The PNEC value is derived for the average surfactant structure based on the relative occurrence of different homologues in the

environment.[77] The comparison of PNEC and predicted environmental concentration (PEC) have been used in the environmental risk assessment of surfactants.[77,78] Table 6 shows some examples of PNEC values for surfactants. It is relevant to notice, that the PNEC value in sewage treatment plant (STP) for SDS is over three orders of magnitude larger than that for didecyldimethylammonium chloride (DDAC).

Table 6. Examples of PNEC values in fresh water, marine water and sewage treatment plant (STP). PNEC values for sodium dodecyl sulphate (SDS), linear alkylbenzenesulphonate (LAS) and didecyldimethylammonium chloride (DDAC) are given.

Surfactant	PNEC			Ref.
	fresh water	marine water	STP	
SDS	137 µg/l	13.7 µg/l	1 084 mg/l	[71]
LAS	320 µg/l	31 µg/l	5.5 mg/l	[78,79]
DDAC	2 µg/l	0.2 µg/l	0.595 mg/l	[73]

5.2.1.1 Biodegradation of surfactants

The breakdown of a chemical through a metabolic pathway of microorganisms is called biodegradation. Several terms are used to describe the different phases of biodegradation. *Primary biodegradation* occurs when the surfactant is cleaved so that it loses surface activity. *Ultimate biodegradation* means the total degradation of surfactant into carbon dioxide, water, inorganic materials and biomass.[6,80] *Ready biodegradation* defined by the Organisation for Economic Co-operation and Development (OECD) indicates rapid biodegradation. A surfactant is defined as readily biodegradable if 60 % biodegradation is achieved within 28 days under aerobic conditions.[6,81] There are multiple tests for ready biodegradation from which the Closed Bottle Test is commonly used for surfactants. If the biodegradation is slower, *inherent biodegradation* tests are used to assess if the compound has any potential for biodegradation in aerobic conditions. At least 20 % biodegradation achieved within the test period is evidence of inherent, primary biodegradability. Over 70 % biodegradation achieved by inherent biodegradation test indicates that the compound can undergo ultimate biodegradation. However, the test duration is not defined for inherent biodegradation tests.[81] In the European Union, it has been set in the Detergent Regulation (EC) No 648/2004 that all surfactants used in detergents must be readily biodegradable.[82]

The rate of biodegradation is highly dependent on surfactant structure and some biodegradation pathways can be predicted on that basis. To biodegrade in the aquatic environment, a surfactant needs to have sufficient water solubility. Very hydrophobic compounds tend to accumulate in lipids of organisms. This is usually not a problem for surfactants itself but their intermediate degradation products are often more hydrophobic, e.g. nonylphenol arising from alkylphenol ethoxylates. Surfactants that have functional groups susceptible to enzymatic hydrolysis, like esters or amides, biodegrade rapidly. The degree of branching and the length of the polyoxyethylene chain in non-ionic surfactants also effect on the biodegradation. Linear fatty alcohols degrade more easily than branched structures. The longer the polyoxyethylene chain, the higher is the overall biodegradation time.[6]

Alkyl sulphates, alkyl ether sulphates, LAS and soaps are all generally readily biodegradable under aerobic conditions.[69,80] However, e.g. hard water and the presence of cationic surfactants can affect to a large extent on the biodegradation. The formation of insoluble calcium and magnesium salts and complexation with cationic surfactants promotes sorption into particulate matter, which results in decreased biodegradation.[80] From the class of non-ionic surfactants, e.g. linear alcohol ethoxylates (with EO content below 20), alkyl polyglucosides and fatty acid esters are generally considered as readily biodegradable.[69,80] Alkylphenol ethoxylates are not readily biodegradable. The degradation products of alkylphenol ethoxylates, e.g. nonyl phenol and octyl phenol have low water solubility and are toxic. Nonyl phenol and octyl phenol are considered as endocrine disrupting compounds which means that they may alter the normal hormone function.[28]

Solid matter is removed from sewage and the obtained sludge is commonly treated under anaerobic digestion. After the treatment, sludge is disposed to agricultural land. Surfactants tend to adsorb on the solid matter. Many surfactants are easily biodegradable under aerobic conditions but the majority cannot degrade under anaerobic conditions. Therefore, after anaerobic treatment, sewage may still contain relatively high amounts of surfactants. For example, LAS and cationic surfactants have a strong tendency to adsorption and show poor anaerobic biodegradation.[80]

As the knowledge about the effects of different surfactants on the environment has increased, some surfactant classes have been replaced by more environmentally benign alternatives. In the 1960s and 1970s, branched alkylbenzene sulphonates were replaced by more biodegradable linear alkylbenzene sulphonates. Dialkyl quaternary ammonium surfactants (dialkyl “quats”) used in fabric softeners were replaced by ester quats during the 1980s and 1990s as ester quats

are easily biodegradable due to the ester group.[6] Alkylphenol ethoxylates have been started to be replaced by alcohol ethoxylates. Restrictions for the use of nonylphenol ethoxylates have been set e.g. in the European Union.[52] Phosphate based detergents were yet widely used in the 1980s, which led to eutrophication in natural waters. Nowadays phosphate based detergent are banned in many countries, e.g. in Europe and various states of US.[70]

5.2.1.2 Skin toxicity of surfactants

In humans, surfactants reach primarily skin because of the extensive use of personal care cleansers.[70,83] Surfactants are known to cause skin irritation. Surfactants are designed to remove hydrophobic materials and can therefore disrupt cellular lipid bilayers. Surfactants interact primarily with the outermost layer of skin, stratum corneum, which is composed of several layers of dead skin cells called corneocytes. The structure of stratum corneum is largely supported by proteins, e.g. keratin filaments. Corneocytes are embedded in a lipid matrix, which contains ceramides, cholesterol, cholesterol esters and free fatty acids. Within corneocytes there are naturally moisturising factors which are biomolecules responsible for hydration of the skin. In addition to removing dirt, oil and sweat from the surface of the skin, surfactants can interact with the proteins and lipids of stratum corneum. Interaction with proteins, especially keratin, causes membrane swelling. The swelling allows excess water to enter corneocytes. After cleansing, the water rapidly evaporates causing drying stresses and the consumer may feel tightness after washing. Surfactants can remove lipids and naturally moisturising factors from stratum corneum. The removal of lipids may happen when the surfactant is applied at concentrations at or above its CMC. Surfactants can also denature proteins and enzymes of the skin and intercalate into the lipid bilayers. Studies have shown that intercalation of surfactants causes loosening in the structure of the lipid matrix and the skin becomes inflamed. Inflammation can be seen as flaking and cracking. When the structure of the skin is damaged, surfactants can penetrate deeper into the skin increasing the irritation. Figure 19 illustrates the effects of surfactants on the skin. Skin irritation can also be induced by residual surfactants left in clothes from laundry detergents.[83]

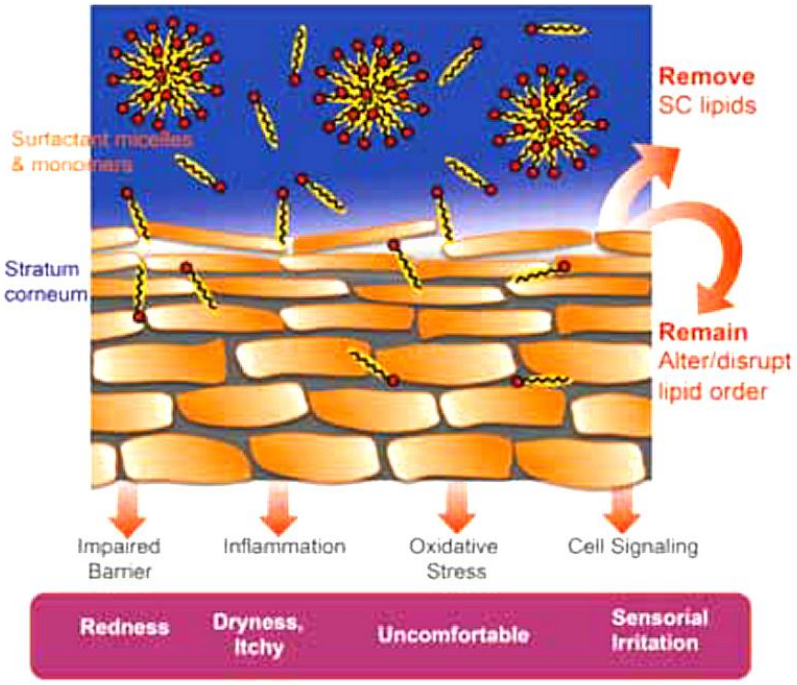


Figure 19. The effects of surfactants on skin.[83]

The first commercial soaps were highly alkaline and were harsh to the skin. Since the 1950s when synthetic surfactants were introduced, research has been carried out to find milder surfactants and to develop mild cleansing formulations.[83] Anionic and cationic surfactants are generally irritating whereas non-ionic surfactants are considered as mild to the skin. [6,83,84] For example betaines, amidobetaines and polyol-based non-ionic surfactants (such as APGs) are very mild to the skin.[6] However, there are exemptions to this rule. When irritancy of different non-ionic surfactants was assessed by tests of cell viability and detection of inflammation markers, PEG ethers appeared to have high skin toxicity.[84] The irritancy potential of anionic and cationic surfactants is related to their ability to bind with proteins of skin. Despite of their relatively high skin toxicity, anionic surfactants are frequently used in personal care products due to their cleansing efficiency and high foamability.[6,83] For example, SDS has relatively high skin irritation potential and it has been used as a reference in skin irritation tests of surfactants.[6,84,85] Along with the ionic group, skin irritancy also depends on the chain length of the hydrophobic tail.[6] In the case of alkyl sulphates, it has been observed that chain lengths C_{12}-C_{15} are more irritating than C_{16}-C_{18}.[86]

Skin irritation problems have been solved by using mixed surfactant systems. The irritancy of surfactants arises from the penetration of surfactant monomers. Therefore, irritancy potential is decreased as the surfactant monomer concentration is decreased and the majority of surfactants in a personal care product exist in micelles.[83] However, surfactant micelles remove lipids from

the skin and it has been discovered that the irritation effect is also related to the stability of micelles.[83,84] By increasing the stability of micelles, less surfactant monomer can penetrate to the skin. The irritancy of anionic surfactants is significantly reduced by adding zwitterionic or non-ionic surfactants. So-called mixed micelles are formed in surfactant mixtures. Mixed micelles are more stable than the micelles of individual anionic surfactant because the charge repulsion is reduced.[83] Tests with humans showed that the mixture of SDS and zwitterionic dimethyl dodecyl amido betaine (DDAB) showed significantly reduced skin irritation even if both surfactants possessed skin irritation in over 80 % of the test group when applied individually. Figure 20 shows, how skin irritancy of SDS/DDAB and SDS/APG mixtures changes as a function of SDS mole fraction.[85]

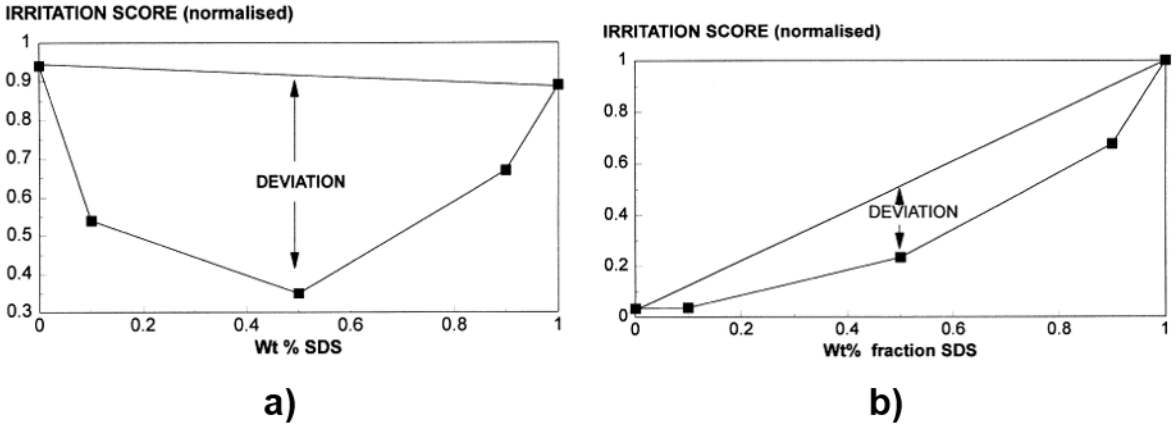


Figure 20. Irritation score vs. mole fraction of SDS for a) SDS/DDAB mixture and b) SDS/APG mixture.[85]

5.3 Paper and board - Compliance for food contact

Food contact materials (FCMs) are defined as "materials and articles intended to come into contact with foodstuffs".[87] FCMs include e.g. packaging materials, machinery in food production, tableware, cutlery and cooking ware.[88] FCMs should be sufficiently inert meaning that considerable amounts of substances are not transferred from FCM into food. FCMs should not either endanger consumer's health or deteriorate the quality of food (composition, taste and aroma). Glass is generally considered as safe material whereas the suitability of plastics needs to be carefully assessed because they include a variety of additives. To protect consumer health, regulations concerning food contact materials have been made. Regulations assess permitted substances and raw materials in FCMs and migration limits or limits of residual content. Migration limit determines the amount of chemical substance that is allowed to diffuse from FCM into food.[89] Several abbreviations appear in the regulations and guidelines that describe

migration and the maximum permitted quantity of a substance.[89,90] Table 7 gives meanings for the most often used abbreviations.

Table 7. Different parameters that describe the maximum permitted quantity of the substance in FCMs or the migration into foodstuffs.[89,90]

Abbreviation	Meaning
QM	The maximum permitted residual amount of a substance in a food contact material
QMA	The maximum permitted residual amount of a substance expressed as mg per 6 dm^2
SML	Specific migration limit; the maximum amount of a specific substance that is allowed to migrate into foodstuffs
SML(T)	Specific migration limit for a group of substances
OM	Overall migration; migration of all non-volatile substances into foodstuffs

5.3.1 Regulation in the European Union

In the European Union, the legislation that covers all FCMs include the Framework Regulation (EC) No 1935/2004 and Regulation on Good Manufacturing Practice (GMP) No 2023/2006.[87,91] The Framework Regulation includes a list of materials and articles, which may be subject to specific requirements. These materials include: Active or intelligent materials, adhesives, ceramics, cork, rubber, glass, ion exchange resins, metals and alloys, paper and board, plastics, printing inks, regenerated cellulose, silicones, textiles, varnishes and coatings, waxes and wood. Active and intelligent materials are intended to extend the shelf life of food and they are not considered as inert as they release substances during preservation into food or absorb substances from food.[87] GMP regulation gives general rules on how food contact materials should be manufactured. The regulation states that every manufacturer should have a quality assurance system by which the compliance of the manufactured food contact material can be ensured. The manufacturer should maintain documentation where all the necessary information including results of quality assurance are presented. These documents are to be available for competent authorities at their request.[91]

After several food crises in the 1990s, the EU adopted Regulation (EC) No 178/2002, known as the General Food Law. In the General Food Law Regulation, it was stated that the risk assessment in food safety issues should be based on scientific knowledge that is independent,

objective and transparent. Under the regulation, European Food Safety Authority (EFSA) was established. EFSA produces scientific opinions and advise on concerning food and feed safety, nutrition, animal health and welfare and plant health and protection. The European Commission, European Parliament and the member states can consult EFSA to help with decision-making on food safety issues.[92,93]

EU is still in the process of harmonising the EU legislation for all types of food contact materials.[94] Currently, there are specific legislation for plastics, active and intelligent materials, recycled plastic materials, ceramics and regenerated cellulose films.[95] No specific regulation for food contact paper and board yet exist in EU level. Therefore, along with the Framework Regulation and the GMP Regulation, EU member states apply national requirements and recommendations for paper and board. In addition, the Council of Europe (CoE) has given instructions for food contact paper and board in Resolution AP (2002) 1. The resolution includes five technical documents where a list of permitted substances and guidelines for compliance testing, good manufacturing practice and the use of recycled fibres in food contact paper and board are given. However, the document is not legally binding.[94]

Following national requirements on specific food contact materials can be problematic, because the requirements may differ from each other. The inconsistency of the national requirements may restrict the free movement of goods, which is the principle in European Union. From the 28 EU member states, nine member states currently have specific measures for food contact paper and board: the Netherlands, Belgium, Germany, the Czech Republic, Slovakia, France, Greece, Croatia and Italy. Typically, the member states have specified in the list of permitted substances fibrous raw materials, fillers, processing/production aids and refining agents. Simoneau *et al.*[88] have reviewed the national/supranational regulations and recommendations applied in EU member states. When the national regulations/recommendations and in paper resolution given by the CoE were compared to each other, it was found that only 9 % of the total substances mentioned were common for two or more member states and the CoE. The widest list of authorised substances was given by the CoE.[88]

German Bundeinstitut fur Risikobewertung (BfR) Recommendations for paper and board used as food contact material are widely accepted in Europe. BfR recommendations either are not legally binding.[94] BfR Recommendation XXXVI (paper and board for food contact) gives lists of approved raw materials, production aids and special paper refining agents in the manufacture of food contact paper and board. Production aids include e.g. sizing agents, retention agents, dispersion and flotation agents and preservatives. For many substances maximum permitted

quantities or specific migration limits are given. The recommendation applies to paper and board used at temperatures up to 90 °C.[96] BfR does not give identification numbers, e.g. CAS number, for the approved substances. However, in the BfR database, CAS numbers are partially included.[97] Special recommendations have given for cooking papers and papers used in hot filtering or extractions (Recommendation XXXVI/1)[98], paper and paperboard for baking purposes at conditions up to 220 °C (Recommendation XXXVI/2)[99] and for absorber pads based on cellulosic fibres for food packaging (Recommendation XXXVI/3)[100]. Recommendation XXXVI/1 is applicable only for paper and board that comes into contact with aqueous food, e.g. tea bags, coffee filters and cook-in-bag packages.[98]

5.3.2 Regulation in the United States

In the Unites States, food contact materials are regulated by U.S. Food and Drug Administration (FDA).[101] The Food Additives Amendment (Section 409) to the Federal Food, Drug, and Cosmetic Act, was given 1958. It stated that all substances defined as food additives must be subject of an applicable regulation. Food additives are defined as substances directly added to food and substances that may become components of food indirectly as migrating from the food contact material. The Food Additives Amendment demanded pre-market approval by FDA for all food additives that were not prior sanctioned or considered Generally Recognised As Safe (GRAS).[102] The approval for food additive is requested through Food Additive Petition (FAP) process, which results in making a new regulation.[103] Regulations concerning food additives are given in Title 21 Code of Federal Regulations, Parts 170-199.[101] Parts 174-179 concern substances used in food contact materials.[103] Substances allowed to use in paper and board intended for food contact are listed in 21 CFR Part 176 “Indirect Food Additives: Paper and Paperboard components”.[94]

In 1997, the regulation of food additives was updated under the Food and Drug Administration Modernisation Act (FDAMA). The FDAMA established a Food Contact Notification process in which a manufacturer or a supplier can apply for FDA approval for new Food Contact Substances (FCS) that are considered as food additives (i.e. can migrate into foodstuffs). The approval applied by FCN is proprietary and effective only for the specific product and use. FDN enables faster approval for new food additives as the review process takes 120 days.[102]

The Food Additives Amendment excluded all the substances that were sanctioned prior to 1958 by FDA or US Department of Agriculture and substances that were generally recognised as safe (GRAS). Substances considered GRAS were generally substances that had already been used

for long in food or in food contact materials. Substances GRAS are listed in 21 CFR Parts 182, 184 and 186. However, not all substances that have the status of GRAS are listed in the regulations. Generally, GRAS status is affirmed by FDA but this is not required by the law. The GRAS status can also be affirmed by scientists or other qualified persons. This has resulted in the existence of substances having GRAS status that are not listed anywhere.[94,104] Also, some non-toxic food contact substances can be exempted by FDA from the petition or notification process if the exposure level is very low, below 1.5 µg per person per day. Requirements for the exemption are given in 21 CFR 170.39 "Threshold of regulation for substances used in food-contact articles".[102,103]

Table 8 shows a few surfactants which have FDA approval for use as a food contact substance. The information has been collected from the FDA database "Substances Added to Food".

Table 8. Examples of surfactants that are listed in FDA regulations: sodium dodecyl sulphate, Tween 20, and polyvinyl alcohol. The approved food contact applications are listed.

Surfactant	CAS	Permission for use
Sodium dodecyl sulphate	151-21-3	Permitted use as a direct food additive: - in coatings on fresh citrus fruit - as an emulsifier or whipping agent in food Permitted use as an indirect food additive in FCMs: - as a component of adhesives and polymeric coatings - in paper and paperboard that come into contact with aqueous, fatty or dry food. - in several polymer materials, e.g. cellophane and textile materials
Tween 20	9005-64-5	Permitted use as a direct food additive: - water boiler additive - flavouring additive Permitted use as an indirect food additive in FCMs: - as a component of adhesives - as emulsifiers
Polyvinyl alcohol	9002-89-5	Permitted use as an indirect food additive in FCMs: - as a component of adhesives and polymeric coatings - in paper and paperboard that come into contact with aqueous, fatty or dry food. - in several polymer materials, e.g. polyvinyl alcohol films may be used in food contact - listed as a prior-sanctioned food ingredient in paper and paperboard used for food packaging

EXPERIMENTAL PART

6 OBJECTIVES

For the development of foam forming technology it is important to know how much surfactant is present in process waters and left in the end product, i.e. the amount of surfactant residues. Surfactant residues are directly related to the recovery of surfactant. Surfactant residues may also effect on the properties of foam-formed products, e.g. strength properties. Before manufacturing of foam-formed products, their safe use must be insured. Paper and board which are used as food contact materials must fulfil the requirements set in national and supranational regulations.[88,94] According to German recommendations given by Federal Institute for Risk Assessment (BfR), migration of alkyl sulphates from the coating of product used for food packaging must not exceed 500 mg/m^2.[105] It also important to consider the capability of surfactants to cause skin and eye irritation.

In this study, methods for quantitative determination of surfactant residues in foam-formed products were developed. Residues of an anionic surfactant, sodium dodecyl sulphate (SDS), and a non-ionic surfactant, Tween 20, were determined from foam-formed hand sheets made in the laboratory. As surfactants were determined from solid samples, sample preparation method played a crucial role. Two determination methods for both surfactants were used to compare different sample preparation procedures and to verify results. SDS residues were determined by solvent extraction spectrophotometry (SES) and inductively coupled plasma optical emission spectroscopy (ICP-OES). For the determination by SES, SDS was extracted in water, whereas in the determination by ICP-OES, ultrasound-assisted nitric acid digestion was used. In addition, the effect of several different parameters on SDS residues were studied: water hardness, water temperature, the presence of non-ionic surfactant and presence of cationic starch. Tween 20 residues were determined by SES and high-performance liquid chromatography equipped with a diode-array detector (HPLC-DAD). As in the determinationof SDS, Tween 20 was extracted in water. In the chromatographic determination, Soxhlet extraction with methanol was used. In addition to the surfactant residues analysis, determination of 4-dodecylbenzene sulphonic acid (here abbreviated 4-DBSA) in water solution by direct UV absorption was also studied. The applicability of the determination methods were assessed using the limit of quantitation (LOQ), possible interfering factors and the practicality of the analysis.

Surfactant residues can be estimated theoretically, when the water content of the product, surfactant dosage and the grammage are known. Theoretical estimation is based on the assumption that surfactant is not chemically adsorbed in the fibre network but is left in the product with water. The experimental values for surfactant residues were compared with the calculated theoretical values to evaluate the behaviour of surfactant in the fibre network. Measured SDS residues were also compared with the migration limit set by BfR. However, this limit is only a limit of migration into food, not a limit of SDS residues. However, if SDS residues are below 500 mg/m^2, exceeding the migration limit is theoretically impossible.

7 MATERIALS AND METHODS

7.1 Reagents and solvents

Table 9 lists all the reagents and solvents used in this study. Ultrapure water was used in the chromatographic determination of Tween 20 and Soxhlet extraction of Tween 20. In all the other experiments, dilutions were made using deionised water.

Table 9. List of reagents and solvents used.

Reagent/solvent	Manufacturer	Purity
Surfactants		
Sodium dodecyl sulphate (SDS)	Sigma-Aldrich	≥ 90 %
Tween® 20	Sigma-Aldrich	Lauric acid ≥ 40 % Water ≤ 3.0 %
4-dodecylbenzenesulphonic acid (4-DBSA)	Aldrich	≥ 95 %
Water hardness adjustment		
Calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$)	Aldrich	98 %
Determination of SDS residues by ICP-OES		
Nitric acid	Fluka	≥ 65 %
Determination of Tween 20 residues by HPLC-DAD		
Ultrapure water	Synergy® water purification system	
Methanol	J. T. Baker	HPLC grade
Methanol	Fisher Scientific	Analytical reagent grade, 99.99 %
Sulphuric acid	Sigma-Aldrich	95.0-97.0 %
Disodium hydrogen phosphate dihydrate ($Na_2HPO_4 \cdot 2H_2O$)	Merck	≥ 99.5 %
Orthophosphoric acid	Merck	≥ 85 %
Orthophosphoric acid	Riedel-de Haën	≥ 85 %
Acetonitrile (ACN)	J. T. Baker	HPLC grade
Acetonitrile (ACN)	Fisher scientific	HPLC grade, 99.99 %
Lauric acid	Fluka	~ 98 %
Extraction experiments		
Ultrapure water	Synergy® water purification system	
Ethanol	Altia	Aa grade, ≥ 99.5 %
Acetone	VWR Chemicals	

7.2 Theoretical estimation of surfactant residues

Surfactant residues in foam-formed products can be estimated from the water content of the product before drying and the amount of surfactant present in the water. The surfactant remains in the product when the water is evaporated. It is assumed that SDS remains in salt form in the product when water is evaporated. Other surfactants are also expected to remain in the product when water is evaporated, and therefore their residues can be estimated by the amount of water and the surfactant dose.

When the surfactant dosage, the dry matter content of the sample before drying and the grammage of the absolute dry sample are known, the theoretical amount of surfactant residues can be calculated as follows

$$\text{Surfactant residues (mg/m}^2) = \left[\frac{1-\text{DM}}{\text{DM}} \cdot \text{GSM}_{\text{dry}}\ (\text{g/m}^2)\right] \cdot\ [\beta\ (\text{g/kg})], \qquad (9)$$

where DM is dry matter content before drying, GSM_{dry} is the grammage of sample and β is surfactant dosage (grams of surfactant per one kilogram (~one litre) of water). The term within the first bracket indicates the amount of water and the term within the second bracket indicates the amount of surfactant in water. Dry matter content is calculated as follows

$$\text{DM} = \frac{m_{\text{dry}}}{m_{\text{wet}}}, \qquad (10)$$

where m_{dry} is the mass of the absolute dry sample and m_{wet} is the mass of the sample before drying.

Figure 21 and Figure 22 present estimate curves for residues of anionic surfactants in the product as a function of dry matter with varying grammage and surfactant dosages. Figure 55 in Appendix 2 presents the theoretical residues of Figure 21 in units of mg/g.

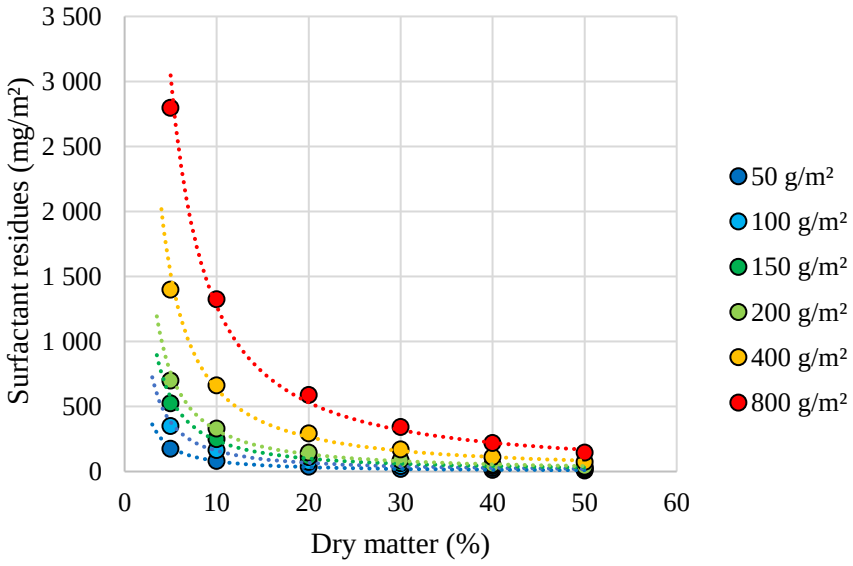


Figure 21. Theoretical residues of an anionic surfactant (mg/m^2) as a function of dry matter content (%) in products having different grammages. The residues have been calculated using constant surfactant dosage of 0.2 g/l.

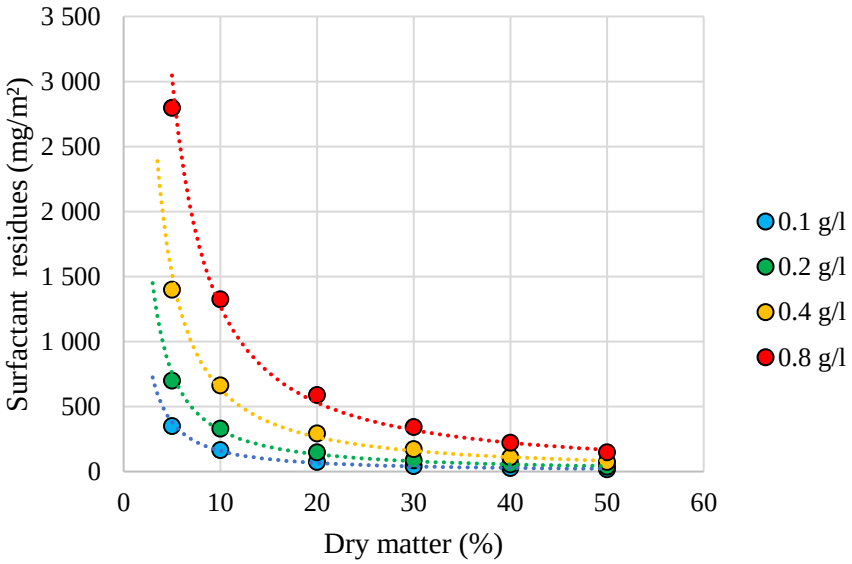


Figure 22. Theoretical residues of an anionic surfactant (mg/m^2) in the product as a function of dry matter (%) at different dosage levels. The residues have been calculated using constant grammage of 200 g/m^2.

7.3 Preparation of foam-formed hand sheets

Foam-formed A4-sized hand sheet samples were prepared using a foam hand sheet mould which is presented in Figure 23b. Target grammage of the sheets was 100 g/m^2. Refined kraft pine pulp was used in the foam generation. The pulp was diluted with deionised water to a consistency of 0.5 %. Adjustment of water hardness was made by adding 6 % $CaCl_2$ solution. The pulp suspension was blended under mild stirring. Foam generation was made by Netzsch Shearmaster, which generates foam by axially agitated mixing (see Figure 23a). The pulp suspension was first weighed into a cylindrical vessel. Next, 10 % SDS solution was added after which foam was generated using a mixing rate of 3650 rpm. When SDS was used as a surfactant, mixing was continued until vortex was closed. In the case of Tween 20, mixing was stopped after 5 min. The obtained foam was poured into a hand sheet mould. When paper-like sheets were prepared, water was removed by vacuum and the obtained sheet was couched. Couching was done by keeping the sheet under 8 kg weight for 30 s. The dry matter content of thin paper-like foam-formed sheets before drying was 20-23 %. When low-density structures were prepared, water was drained first by the influence of gravitation for 10 min, which results in very bulky and wet structure (see Figure 23c). After the drainage, the dry matter content was 4.5-5.5 %. The residual water was removed by evaporation in an oven at 70 °C. Convection was not used.

a)  b)  c) 

Figure 23. Preparation of foam-formed samples: a) foam generation by Netzsch Shearmaster agitator, b) foam hand sheet mould and c) foam-formed bulky low-density structure.

Dry matter contents of thin paper-like samples were determined after couching. After couching, the edges of a wet sheet were carefully removed and the wet sheet was weighed. The sheets were dried in Lorentzen & Wettre rapid dryer and weighed after drying. Dry matter contents of bulky samples were determined immediately after the drainage. A proper amount of sample was collected with a bucket from the hand sheet mould into a tared container and weighed. The sample was filtered and the fibres were dried in a rapid dryer and weighed after drying.

7.3.1 Samples

Table 10 shows the samples prepared for the determination of SDS residues by spectrophotometry and ICP-OES. Water hardness of the suspension was adjusted to °dH = 5. The effect of SDS dosage, dry matter content before drying and drying method were studied. Paper-like sheets were dried either at air over night or in a rapid dryer for 15 min. Rapid drying was studied to find out if the surfactant residue analysis and the determination of dry matter content could be done from the same sample.

Table 10. The samples prepared for the determination of SDS residues by spectrophotometry and ICP-OES. Water hardness of the suspension was adjusted to °dH=5.

Water removal	SDS dosage (g/l)	Average DM before drying (%)
1. Drainage by vacuum 2. Air drying over night	0.4 0.6 1.2 1.8 2.4	~ 23
1. Drainage by vacuum 2. Rapid drying 15 min	0.4 0.6 1.2 1.8 2.4	~ 23
1. Drainage by the influence of gravitation 10 min 2. Drying in an oven at 70 °C for over night	0.4 0.6 1.2 1.8 2.4	~ 5

Table 11 shows the samples prepared for the determination of Tween 20 residues. Water hardness was adjusted to °dH = 5. Thin paper-like sheets and bulky low-density sheets were prepared.

Table 11. The samples prepared for the determination of Tween 20 residues. Water hardness of the suspension was adjusted to °dH=5.

Water removal	Tween 20 dosage (g/l)	Average DM before drying (%)
1. Drainage by vacuum 2. Air drying over night	6 9 12	21.0
1. Drainage by the influence of gravitation 10 min 2. Drying in an oven at 70 °C for over night	6 9 12	5.5

Table 12 describes the samples used to study the effect of water hardness, water temperature and the addition of cationic starch on SDS residues. All the samples were thin paper-like sheets, which were dried at air. By water hardness °dH = 0, it is meant that the pulp was diluted with deionised water without adding any $CaCl_2$. In the temperature experiments, the suspension was

heated to 50 °C before foaming. The cationic starch charge was 20 kg per dry tonne of fibres in the pulp suspension. 10 g/l starch solution was prepared in deionised water. The solution was heated in a decanter covered with folio to 97 °C and kept at that temperature for 30 min. The starch solution was stored at 70 °C and used within one day after preparation.

Table 12. The samples prepared to study the effect of water hardness, water temperature and the addition of cationic starch on SDS residues. All the samples were thin paper-like sheets (water removal by vacuum followed by air drying).

Preparation conditions	SDS (g/l)	Average DM before drying (%)
▪ °dH = 5	0.4 0.6 1.2 1.8 2.4	21.4
▪ °dH = 0	0.6 1.2 2.4	20.0
▪ °dH = 5 ▪ water temperature 50 °C	0.4 0.6 1.2 1.8 2.4	21.6
▪ °dH = 5 ▪ Addition of cationic starch 20 kg/t	0.4 0.6 1.2 1.8 2.4	21.8

Table 13 describes the samples prepared to study the effect of Tween 20 addition on SDS residues. All the samples were thin paper-like sheets dried at air. Water hardness of the pulp suspension was °dH = 5. The same SDS dosages were used as in the earlier experiments. Tween 20 was added using the following ratio,

$$c(\text{Tween 20})(\text{mol/l}) = 0.3125 \cdot c(\text{SDS})(\text{mol/l}), \quad (11)$$

where $c(\text{Tween 20})$ is the concentration of Tween 20 (mol/l) and $c(\text{SDS})$ is the concentration of SDS (mol/l). This particular molar ratio was used because in the earlier studies, the foaming characteristics were observed to be desirable with this ratio. In addition, one sample was prepared with a triple amount of Tween 20 to see if the amount of non-ionic surfactant has an

effect on SDS residues. Two samples were also prepared by heating the suspension to temperature of 50 °C.

Table 13. The samples prepared to study the effect of the addition of Tween 20 on SDS residues. All the samples were thin paper-like sheets (water removal by vacuum followed by air drying).

Preparation conditions	SDS dosage (g/l)	Tween 20 (g/l)	Average DM before drying (%)
▪ °dH = 5 ▪ Addition of Tween 20	0.4 0.6 1.2 1.8 2.4	0.5 0.8 1.6 2.4 3.2	21.2
▪ °dH = 5 ▪ Addition of 3x amount of Tween 20	0.6	2.4	20.8
▪ °dH = 5 ▪ Addition of Tween 20 using the ratio Tween 20 0.5 mmol/l + SDS 1.6 mmol/l ▪ Water temperature 50 °C	1.2 1.8	1.6 2.4	22.0

7.4 ICP-OES

7.4.1 Instrumentation and sample preparation

In this study, PerkinElmer Optima 8300 DV ICP-OES was used for the determination of SDS residues. The instrument is presented in Figure 24. The instrument was equipped with 40 MHz FlatPlate RF generator, a GemCone Low-Flow nebuliser and a cyclonic spray chamber.

Figure 24. PerkinElmer Optima 8300 instrument.

Before the analysis, the samples were prepared using ultrasound-assisted nitric acid digestion. Bandelin Sonorex ultrasonic bath was used in the digestion. Approximately 0.5 g of sample was accurately weighed and torn to pieces of approximately 1 cm x 1 cm. The pieces were moved into a 50 ml stoppered plastic tube and 10 ml of concentrated nitric acid was added. The tubes were closed and placed in the ultrasonic water bath. Samples were sonicated for 3 x 3 min. After each cycle, stoppers were opened to let the pressure come out. After sonication, the samples were filtered through ashless filter paper with a pore size of 20-25 µm (Whatman 41) and diluted to 50 ml volume.

SDS residues were determined by measuring sodium and sulphur content. A foam hand sheet prepared using Tween 20 as a surfactant served as a blank sample. First, semiquantitative measurements were performed to find out the concentration levels. Calibration solutions were prepared based on the semiquantitative measurements and a quantitative measurement method for sodium and sulphur was created. Sodium and sulphur calibration solutions were prepared from stock solutions with 2 % nitric acid background. The sodium stock solution had been prepared from sodium chloride and the sulphur stock solution from ammonium sulphate in deionised water. Sodium was measured at 589.592 nm. Sulphur was measured at 181.975 nm and at 180.669 nm. The radial measuring view was used in the determination of sodium and axial measuring view in the determination of sulphur. The sample introduction system was flushed between every sample with 5 % nitric acid. The measurement parameters used in the quantitative measurement are presented in Table 14.

Table 14. Measurement parameters used in ICP-OES for the determination of sodium and sulphur.

Measurement parameters	
RF power	1500 W
Outer argon flow	8 l/min
Intermediate argon flow	0.2 l/min
Inner argon flow	0.6 l/min
Sample flow rate	1.50 ml/min
Measuring view	Radial (Na)
	Axial (S)

7.5 Determination by solvent extraction spectrophotometry

7.5.1 Sample preparation

For the spectrophotometric determination, SDS was extracted from the solid sample in deionised water. Depending on the amount of SDS residues, approximately 0.5-1.0 g of sample was weighed and torn to pieces. The sample was disintegrated in approximately 400 ml of deionised water by hand blender. The mixture was filtered two times to get a clear solution that did not contain any fibres, firstly with ashless filter paper having 8 µm pore size (Whatman 40) and finally using mixed cellulose ester membrane (ME) filter with 0.45 µm pore size (Whatman ME 25). Finally, the filtrate was diluted to a volume of 1 litre.

7.5.2 Instrumentation

The spectrophotometric determination of SDS and Tween 20 is based on solvent extraction. The determination was carried out by Hach Lange DR3900 VIS spectrophotometer using Hach Lange LCK cuvette test system. The spectrophotometer is a simple benchtop spectrophotometer equipped with RFID-technology. The idea of LCK cuvette test system is to reduce sample preparation steps and the amount of reagents used in the analysis by using pre-dosed cuvettes. The cuvette tests are designed to be used in water analysis. When the cuvette is placed in the spectrophotometer, it recognises the test by the barcode label and selects the correct measuring wavelength automatically. The spectrophotometer also includes calibration for every LCK test. There are LCK cuvette tests available for a variety of water analyses, e.g. for the determination of COD (chemical oxygen demand), phosphate and ammonia. LCK cuvette tests also include tests for quantitative determination of anionic, cationic and non-ionic surfactants.[106,107] The spectrophotometer and LCK cuvette tests are presented in Figures 25a and b.

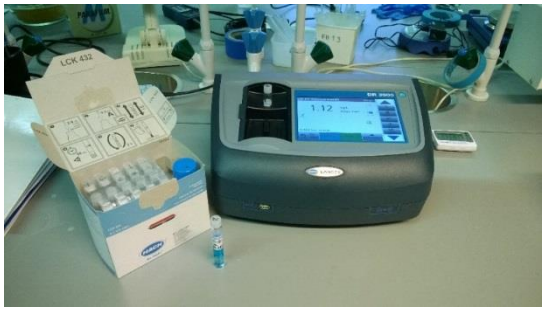
a)  b) 

Figure 25. a) Hach Lange DR3900 VIS spectrophotometer and LCK432 cuvette tests for anionic surfactants. b) LCK433 cuvette test for non-ionic surfactants.

The used LCK cuvette tests in the determination of SDS and Tween 20 and the working procedures are described in Table 15. LCK432 cuvette test for anionic surfactants was used for the determination of SDS. The test is based on the methylene blue method. Anionic surfactant and methylene blue form a complex that is extracted in chloroform. The procedure of the test is simple; 2 ml of the sample solution and 200 µl of dye solution are added into the cuvette. The screw top is closed and the cuvette is shaken for 1 min. The phases are let to separate after which the absorbance can be measured. The absorbance of the chloroform phase measured at 650 nm. Measuring range of LCK432 test given by the manufacturer is 0.1-4.0 mg/l (0.1-4 ppm). Because the calibration included in the spectrophotometer has been made using another surfactant (sodium dodecylbenzenesulphonate), the results given by the spectrophotometer do not apply to SDS. Therefore, calibration with SDS water solutions was performed.

LCK433 and LCK333 tests for non-ionic surfactants were used for the determination of Tween 20. The tests can be applied for non-ionic surfactants containing 3-20 ethylene oxide units. The tests are based on forming a complex with TBPE (tetrabromphenolphthaleinethylester) that is extracted in dichloromethane. The absorbance is measured at 606 nm. The difference between the tests is the measuring range. The measuring ranges of LCK333 and LCK433 tests are 0.2-6.0 mg/l and 6.0-200 mg/l, respectively. The manufacturer has used Triton X-100 in the calibration of the spectrophotometer, thus, like in the case of SDS, a calibration curve was made for Tween 20.

Table 15. Descriptions of the used LCK cuvette tests. Name of the test, dye reagent, measuring range and the working procedure are described.

Test	Dye reagent	Measuring range*	Working procedure
LCK432 for anionic surfactants	Methylene blue	0.1-4.0 mg/l	Add 2 ml of sample and 200 µl of dye solution. Shake 1 min and let the phases separate.
LCK333 for non-ionic surfactants	TBPE	0.2-6.0 mg/l	Add 2.5 ml of sample. Shake 2 min vigorously and let the phases separate.
LCK433 for non-ionic surfactants	TBPE	6.0-200 mg/l	Add 200 µl of sample. Shake 2 min vigorously and let the phases separate.

* Measuring range applies only for the calibration made by the manufacturer.

7.6 HPLC-DAD

Tween 20 was extracted from foam-formed hand sheets by Soxhlet extraction followed by chromatographic analysis with HPLC-DAD. The chromatographic analysis was performed similarly like in the study of Őszi *et al.*[108], except that in this study, gradient program instead of the isocratic program was used. The analysis is based on acidic hydrolysis of Tween 20. When acidic hydrolysis is performed, Tween 20 decomposes and lauric acid is formed. Lauric acid absorbs UV radiation and can be detected at 210 nm. The hydrolysis reaction and the structure of lauric acid are presented in Figure 26. Calibration was performed with hydrolysed Tween 20 standard solutions. Tween 20 is supplied as a relatively unpure reagent, because fatty acid mixtures are used in the production. According to the manufacturer, ≥ 40 % of the fatty acid content in Tween 20 is lauric acid. Other fatty acids are primarily myristic, palmitic and stearic acid. Therefore, a calibration with pure lauric acid was also performed to determine the lauric acid content in Tween 20. To determine Tween 20 by detection of lauric acid, the lauric acid content in Tween 20 must be constant.

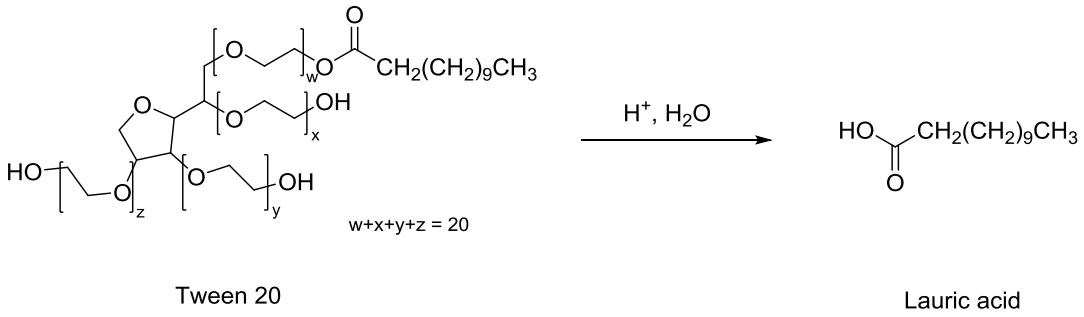


Figure 26. Acidic hydrolysis of Tween 20. Lauric acid is formed as a decomposition product.

7.6.1 Sample preparation

A conventional Soxhlet extractor with 100 ml extraction head was used. Methanol was used as the extraction solvent. The extraction apparatus was performed as follows. Cellulose extraction thimbles, cotton wool, boiling chips and all the glassware used were washed with methanol before the extraction. The extraction thimbles were sonicated in methanol for 15 min. Approximately 1.0 g of accurately weighed air-dry sample was placed into an extraction thimble. The head of the extraction thimble was blocked by cotton wool. The thimble was placed inside the extraction head. Next, 200 ml of methanol was placed into a distillation flask and a few boiling chips were added. The extraction head and distillation flask were connected with a condenser. The temperature was adjusted so that the extraction head drained 6-10 times per hour. The extraction time was 4 h. Figure 27a shows the Soxhlet extraction set-up.

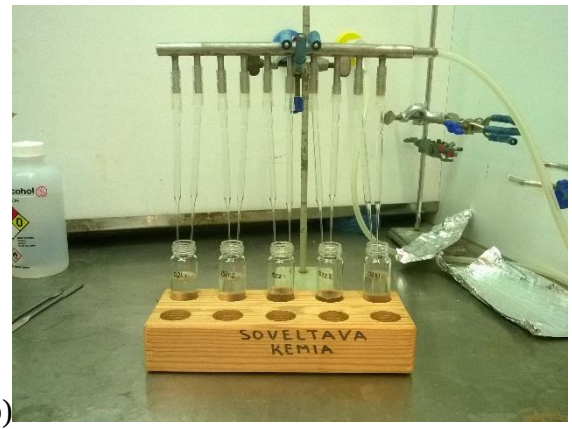
a)  b) 

Figure 27. Pictures of a) the Soxhlet extraction set-up, and b) evaporation of sample extracts by nitrogen flow.

After the extraction, the obtained extracts were evaporated almost to dryness. The concentrate was moved into a 30 ml tared glass tube. The glass tubes had been dried without screw tops at 105 °C for 30 min to ensure there is no moisture inside. The distillation flask was carefully washed with methanol and the wash solutions were combined with the extract. The extracts were evaporated to dryness by nitrogen flow (Figure 27b). After 24 h, the extracts were weighed. The evaporation was continued until the mass of the extract no longer changed. The dried extracts were stored in a fridge.

Throughout the study, all the standards and samples analysed by HPLC-DAD, were diluted in 1:2 (v/v) water/acetonitrile mixture. Lauric acid standard solutions were prepared in 1:2 (v/v) water/acetonitrile solution. Tween 20 standard solutions were prepared in ultrapure water. The hydrolysis was performed using sulphuric acid. 1 ml of Tween 20 standard solution and 1 ml of 4 M sulphuric acid were placed in a 10 ml stoppered glass tube and the tube was shaken thoroughly. After approximately 24 h reaction time, 4 ml of acetonitrile was added and the solution was shaken until all the decomposition products were dissolved. Hydrolysis of the sample extracts was performed in the same manner. The dried extract was dissolved in 2 ml of water and 2 ml of 4 M sulphuric acid was added. After approximately 24 h, 8 ml of acetonitrile was added. Before the analysis, all the standards and samples were filtered through 0.45 µm PVDF membrane filter.

7.6.2 Instrumentation

Hewlett-Packard 1100 Series HPLC was used in the chromatographic determination of Tween 20 (Figure 28). The HPLC was equipped with a binary pump, autosampler and diode-array detector. Gemini C18 reversed phase column (100 x 4.6 mm) with a particle size of 3 µm and

initial column were used in the separation. 0.020 M Na_2HPO_4 buffer (pH = 2.8) and acetonitrile were used in the mobile phase. New phosphate buffer was prepared every day to prevent bacterial growth. pH was adjusted to 2.8 with phosphoric acid. Phosphate buffer solution was filtered through a 0.45 µm ME membrane filter. Before injecting into the lines, buffer solution and acetonitrile were degassed with helium for a few minutes.

Figure 28. Hewlett-Packard 1100 Series HPLC.

The measurement parameters used in the experiments are presented in Table 16. The column temperature was kept at 30 °C to ensure that the samples remain in the liquid state. The flow rate was 0.8 ml/min and the run time 19 min. The gradient program used in the measurements is presented in Figure 29. The run was started at 65 % where it was kept for 1 min. The portion of acetonitrile was increased linearly to 80 % over the next 3.5 min and was kept there for 8.5 min. Then, the portion of acetonitrile was decreased back to 65 % over the next 1 min and was kept there for 5 min. 1:2 (v/v) water/acetonitrile solution was used as a washing solution for the injection needle. Lauric acid was detected at 210.8 nm.

Table 16. The measurement parameters used in the chromatographic determination.

Measurement parameters	
Column	Gemini C18, 3 µm pore size, 100 x 4.6 mm
Mobile phase	Gradient
	A) 0.020 M Na_2HPO_4 buffer, pH 2.8
	B) ACN
Column temperature	30 °C
Flow rate	0.8 ml/min
Injection volume	20.0 µl
Run time	19 min
Detection wavelength	210.8 nm

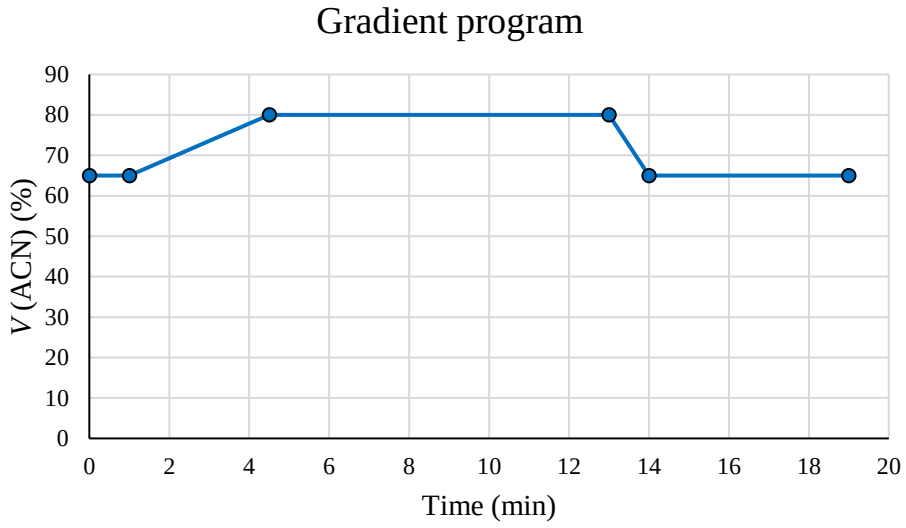


Figure 29. The gradient program used in the chromatographic determination.

7.7 UV-absorption

Different compounds absorb light at different wavelengths. The wavelength of maximum absorbance λ_{max} is a characteristic value, which arises from the structure of the compound. The molar absorptivity ε describes how strongly a chemical compound absorbs light at a specific wavelength. According to Beer-Lambert law, the molar absorptivity is defined as

$$\varepsilon = \frac{A}{cl}, \tag{12}$$

where A is the absorbance, c is the concentration of the absorbing compound in mol/l and l is the path length of light in cm. As absorbance is a dimensionless quantity, the molar absorptivity is expressed in units of $M^{-1}cm^{-1}$.[41]

As mentioned earlier (Chapter 4.2), LAS can be determined by direct UV-absorption.[3] This method was tested for the determination of 4-DBSA in water solution. Quartz cuvettes with 10 mm path length were used in the measurements. To determine the absorbance maximums for 4-DBSA, wavelength scan measurements were conducted with standard solutions by PerkinElmer Lambda 25 UV/VIS-spectrophotometer. Reference cell that contained deionised water was used in the measurements. The absorbance maximums were determined, after which absorbance measurements at those wavelengths were performed and the calibration curves were established. Reference absorbance measurements were also conducted by Hitachi U-2900 UV/VIS-spectrophotometer.

7.8 LOD and LOQ

Limit of detection (LOD) is defined as the concentration which gives a signal that significantly different from the blank signal. *Significantly different* means that the signal is three times higher than the background noise. LOD can be estimated from the calibration curve and is calculated as follows

$$LOD = y_B + 3s_{y/x}, \tag{13}$$

where y_B is signal of the blank and $s_{y/x}$ is the standard error of the intercept. When the measured concentration is above LOD, it can be said that the analyte is present. However, it cannot be quantitatively determined. It has been suggested that for a quantitative measurement, the signal must be ten times higher than the background noise. Limit of quantitation (LOQ) is the lowest concentration that can be measured with acceptable accuracy.[109] LOQ is calculated as follows

$$LOQ = y_B + 10s_{y/x}. \tag{14}$$

8 RESULTS AND DISCUSSION

8.1 Determination of SDS residues by ICP-OES and SES

Dry matter contents of samples before drying were determined. It was noticed that dry matter content decreased as the dosage of SDS increased. However, dry matter content varies little as a function of dosage, so the theoretical SDS residues were calculated using dry matter content of 23 % for samples made using a vacuum and dry matter content of 5 % for samples made without vacuum.

The calibration of ICP-OES succeeded. The correlation coefficients (R^2) were > 0.999. Two different calibration ranges were used in the measurements. First, standard concentrations of 0.25, 2.5 and 25 mg/l for sodium and sulphur were used. Later, a standard concentration of 250 mg/l was added when it was noticed that the concentrations of some samples were above the calibration range. Because ICP-OES measures the amount of elements, this has to be taken into account when measuring the amount of SDS residues in the foam-formed samples. A foam-formed hand sheet made using Tween 20 as a surfactant served as the "blank" sample. The blank sample was used to determine sulphur content of the pulp. When calculating results, sulphur content of the pulp was subtracted from the results. The results were calculated using

both sodium and sulphur concentrations. It was discovered that results calculated from sulphur content corresponded the results of colorimetric determination much better. The wavelength of 180.669 nm for sulphur was used to calculate the amount of SDS residues, because it gave higher intensities compared to 181.975 nm. Figure 30 presents the calibration curves of sulphur (180.669 nm). Calibration curves of sodium (589.592 nm) and sulfur (181.975 nm) and the results of the determination of SDS residues by ICP-OES are presented in Appendix 3.

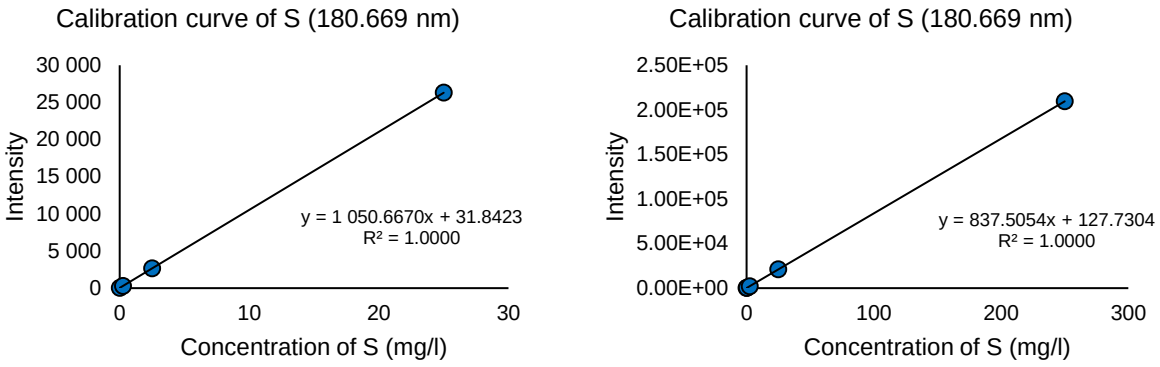


Figure 30. Calibration curves for the determination of S (180.669 nm) by ICP-OES. In the left, concentrations of standards are 0.25, 2.5 and 25 mg/l. In the right, concentrations of standards are 0.25, 2.5, 25 and 250 mg/l.

Figure 31 shows the calibration curve for the spectrophotometric determination of SDS. The results of the spectrophotometric determination of SDS residues are presented in Appendix 4.

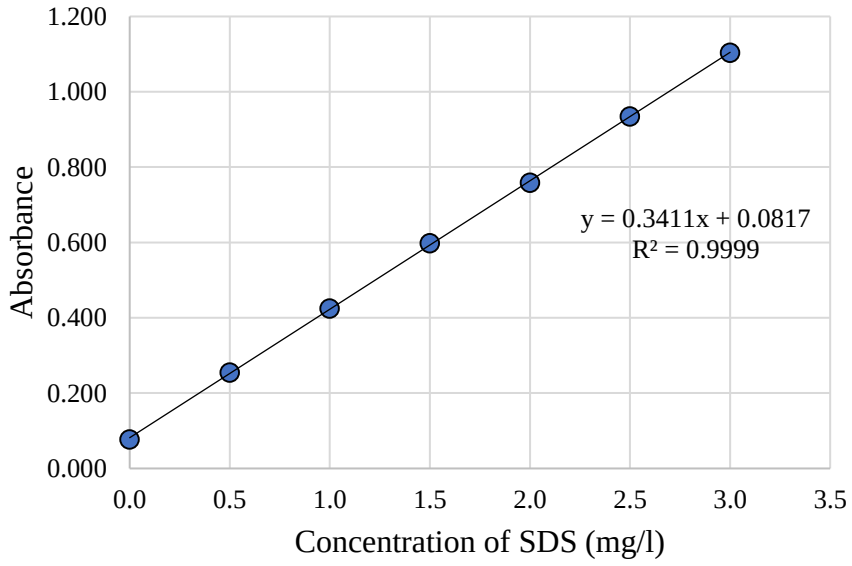


Figure 31. Calibration curve for the colorimetric determination of SDS. The graph shows absorbance as a function of SDS concentration (mg/l). The equation of calibration curve is $y = 0.3411x + 0.0817$ and the correlation coefficient $R^2 = 0.9999$.

Known concentrations of SDS in water solutions were also determined by ICP-OES. The concentrations of 50, 500 and 1000 mg/l were prepared from 10 % SDS stock solution in deionised water. The measured SDS concentrations were calculated from sulphur concentrations and are presented in Table 17. The results show that measured concentrations are higher than prepared concentrations. The ratio of measured concentration to prepared concentration seems to increase as the concentration decreases. This may be due to increase in dilution error. The purity of the used SDS powder was only ≥ 90%. The fact that measured concentrations are higher than prepared indicate that there are sulfur-containing impurities in the commercial SDS powder. Sodium sulphate is one of the major inorganic impurities in anionic surfactants.

Table 17. SDS concentration in water solutions determined by ICP-OES. The table shows prepared and measured concentrations (mg/l) and the ratio of measured concentration to prepared concentration.

$c_{prepared}$ (mg/l)	$c_{measured}$ (mg/l)	Ratio (measured/prepared)
50	74	1.47
500	640	1.28
1000	1240	1.24

Figure 32 shows measured SDS residues in air-dried samples with the theoretical values as a function of SDS dosage. The measured results deviate significantly from theoretical values. It seems that the measured values are close to the theoretical values up to a dose level of 0.5 g/l. After that, the measured values are higher than the theoretical values. At the dosage of 1.8 g/l measured residues are over twice the theoretical value. Therefore, it seems that anionic surfactant is adsorbed to the fibrous network. Solvent extraction spectrophotometry detects only surface active molecules. What stands out from Figure 32 is that ICP-OES and spectrophotometric determination give very similar results. Therefore, we might assume that SDS molecules are not degraded during the drying phase. Another important finding was that the water extraction of SDS from foam-formed hand sheets works and the spectrophotometric determination method (which is targeted to surfactant solution) could also be applied to solid foam-formed samples. Estimation of SDS residues based on the water content of the product before drying and amount of surfactant present in the water is possible only at small SDS dosages.

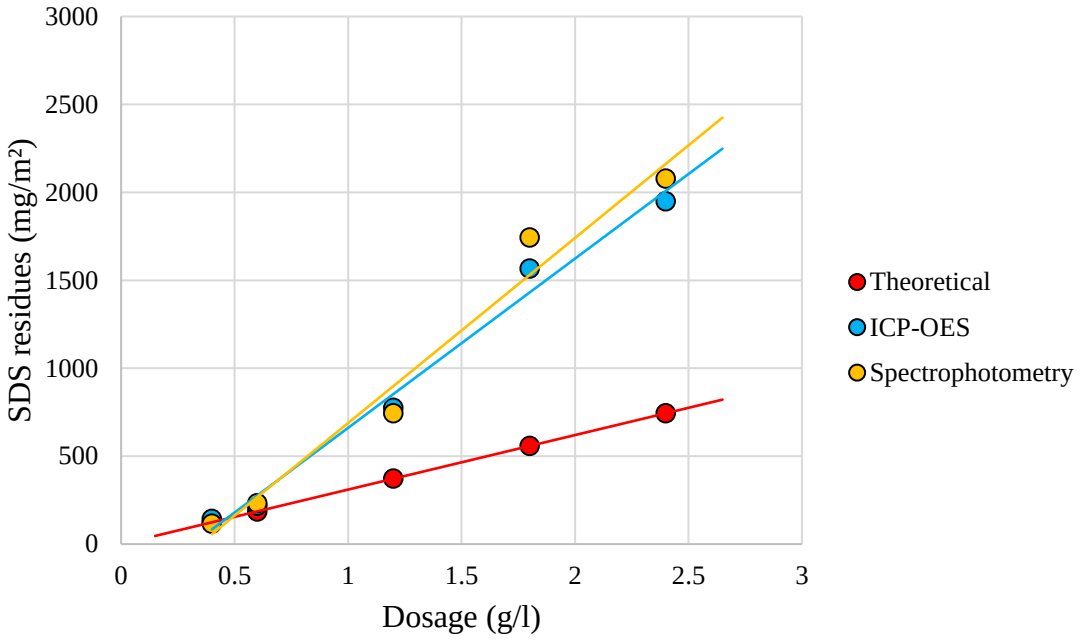


Figure 32. SDS residues in foam-formed hand sheets made by vacuum and dried at air. The graph shows SDS residues (mg/m^2) as a function of SDS dosage (g/l). Some of the data points are average values of replicate samples. A graph that shows SDS residues in units of mg/g is presented in Appendix 5 (Figure 57).

Figure 33 shows SDS residues in rapid dried samples as a function of SDS dosage. In this case, the measured SDS residues are below the theoretical values. The results of the two determination methods (ICP-OES and spectrophotometric) have the same trend although there is more deviation between replicate samples than in the air-dried samples. The lower amount of SDS residues in rapid dried samples is probably caused by the use of suction boards. Water and SDS with it is absorbed into suction boards, which results in lower SDS residues in the sample. Use of suction boards is a necessity when samples are dried using the rapid dryer. Suction boards are used in rapid drying to protect a hand sheet from damages caused by contact heat and to prevent fibres from adhering to the hot surface of drier. SDS can also be left on the interiors of the rapid dryer.

The recommended procedure is therefore to analyse two samples. From one sample, the grammage is determined (this can be done using rapid dryer) and from the second sample, after disintegration in water, the SDS content is determined.

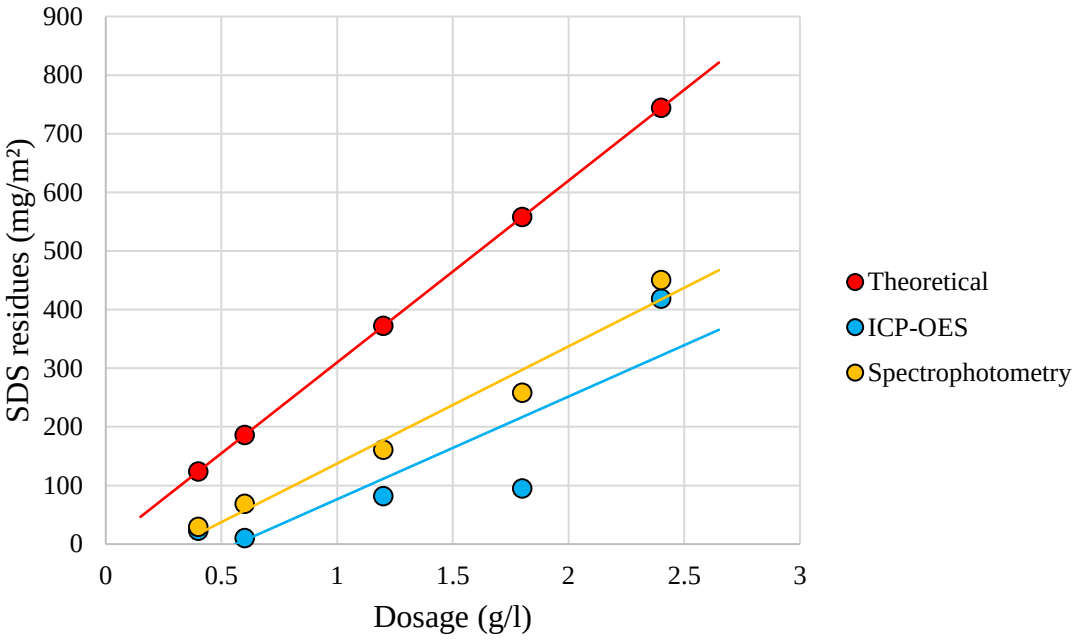


Figure 33. SDS residues in foam-formed hand sheets made by vacuum and dried in a rapid dryer. The graph shows SDS residues (mg/m^2) as a function of SDS dosage (g/l). Some of the data points are average values of replicate samples.

Figure 34 shows SDS residues in bulky low-density samples (drainage without vacuum followed by drying in an oven) as a function of SDS dosage. One should notice that samples were very wet before oven drying (dry matter contents of samples were below 6%). When determining dry matter contents, it was also noticed that dry matter content (before drying) decreased as the dosage of SDS increased. The dry matter content of a sample made with the dosage of 0.4 g/l was 5.83 % and the dry matter content of a sample made with the dosage of 2.4 g/l was 4.50 %.

One should notice that in Figure 32 the maximum value of SDS residues was about 2000 mg/m^2. However, in Figure 34 the smallest measured SDS residues were above that value. The SDS dosages were similar in both cases. The difference is due to the difference in dry matter content. The amount of water and therefore the amount of surfactant was greater in bulky low-density samples.

Figure 34 shows that measured SDS residues are much higher than the estimated, theoretical values at every SDS dosage level. As expected, it was observed that SDS residues increased as the SDS dosage increased. It is very interesting to notice that a drop in measured values is observed at the dosage of 2.4 g/l which is above the critical micelle concentration (CMC) of SDS. Also, the extent of increase as a function of SDS doses in the measured SDS residues was greater in air-dried samples than in bulky low-density samples. Figure 35 presents measured

SDS residues in air-dried samples and bulky low-density samples as a function of theoretical surfactant residues in units of mg/g. It can be seen from the Figure 35 that dependence between the measured residues and the theoretical residues is linear ($R^2 > 0.95$) and measured residues are about triple compared to the theoretical ones. The highest measured value was close to 100 mg/g (see Figure 35). If one gram of sample were disintegrated in one litre of water, the SDS concentration of the suspension would be about 100 ppm (100 mg/l). This kind of suspension can be foamed without adding more surfactant.

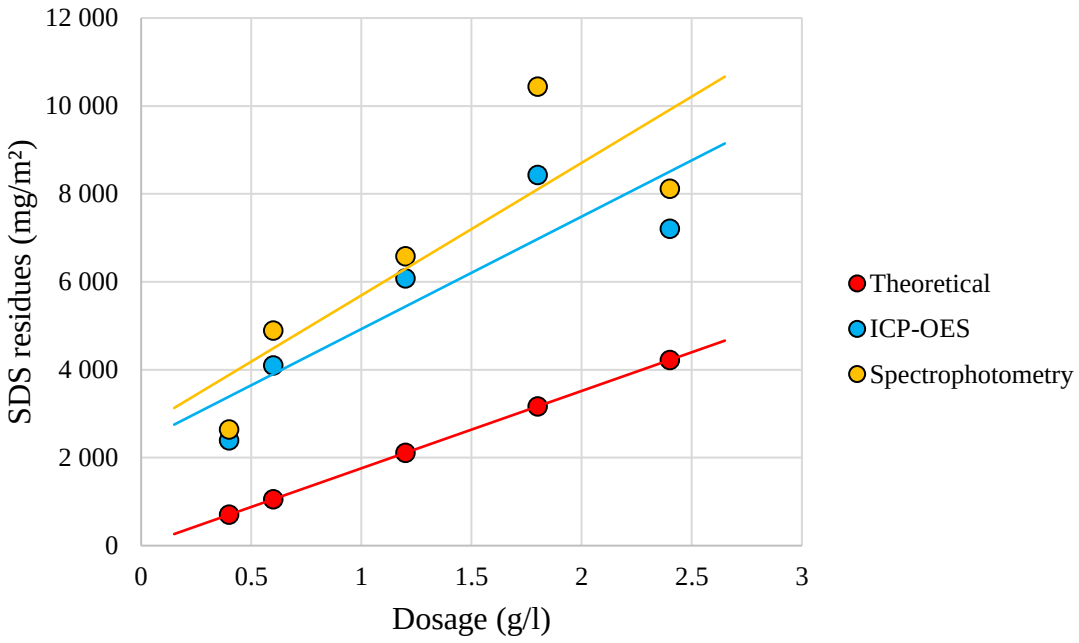


Figure 34. SDS residues in foam-formed hand sheets made without vacuum and dried in an oven at 70 °C. The graph shows SDS residues (mg/m^2) as a function of SDS dosage (g/l). Some of the data points are average values of replicate samples. A graph that shows SDS residues in units of mg/g is presented in Appendix 5 (Figure 58).

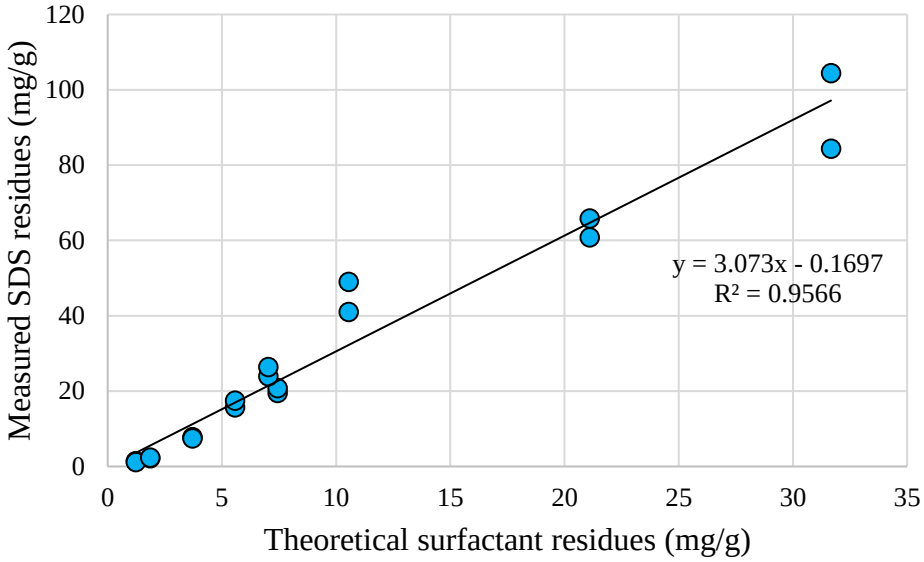


Figure 35. Measured SDS residues (mg/g) in foam-formed hand sheets as a function of theoretical surfactant residues (mg/g). The results that correspond to theoretical values below 40 mg/g are presented.

8.2 The effect of water hardness, temperature, cationic starch and non-ionic surfactant on SDS residues

After it was discovered that SDS residues are left in the fibre network more than theoretically estimated, it was studied which parameters affect the amount of residues. Many anionic surfactants, like alkyl sulphates and carboxylates of fatty acids, precipitate as salts with divalent and trivalent cations, such as calcium, magnesium, barium and iron.[1,3,110] Therefore, it was investigated if the salt formation have an influence on the high amount of SDS residues.

Figure 36a and Figure 36b present the measured SDS residues and the corresponding theoretical residues as a function of SDS dosage when water hardness is °dH = 0 and when water hardness is °dH = 5 and the temperature of the suspension is 50 °C, respectively. The graphs show that the measured SDS residues are now at the theoretical level. It can be concluded that SDS residues decrease when water hardness decreases or when the temperature increases. Previously the measured SDS residues were higher than the theoretical values due to the formation of an insoluble salt with Ca^{2+} ions. Calcium and magnesium salts of dodecyl sulphate are very insoluble.[111] The solubility of calcium dodecyl sulphate $Ca(DS)_2$ is only 0.461 mmol/l (0.14 g/l) at 25 °C. The Krafft point (i.e. the temperature at which the solubility of a surfactant increases enormously) of $Ca(DS)_2$ is 50 °C where the solubility of $Ca(DS)_2$ is 1.62 mmol/l (0.49 g/l). Throughout the studies, water hardness was adjusted by adding $CaCl_2$ so only calcium ions

were present. The definition of German degree of water hardness is that one degree °dH = 1 corresponds to 10 mg/l of calcium oxide. Thus, there were 0.89 mmol/l Ca^{2+} ions in the suspension. This value is below the maximum solubility of $Ca(DS)_2$ at 50 °C. As the temperature is increased the solubility of $Ca(DS)_2$ increases and at 50 °C there is no salt present in the suspension.

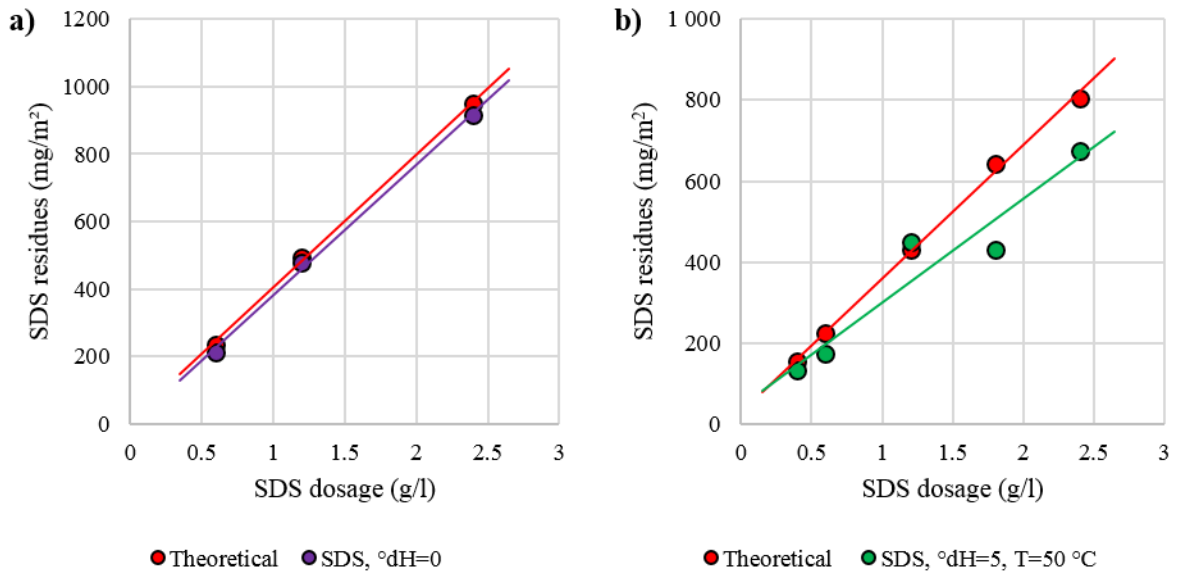


Figure 36. SDS residues a) when water hardness is °dH=0 and b) when water hardness is °dH = 5 and the temperature of the fibre suspension is 50 °C. The graphs show measured SDS residues and the corresponding theoretical values (mg/m^2) as a function of SDS dosage (g/l).

Figure 37 shows measured SDS residues when a mixture of SDS and Tween 20 was used in the foam generation in water hardness of °dH = 5. It can be seen from Figure 37 that when Tween 20 is added, SDS residues decrease. However, by increasing the temperature to 50 °C no further decrease in SDS residues is observed. One sample was made using a triple amount of Tween 20. Increasing the amount of Tween 20 neither did further decrease the amount of SDS residues.

The decrease of SDS residues by the addition of Tween 20 is due to the formation of mixed micelles. In the mixture of SDS and Tween 20, SDS is bound in the micelle structures with Tween 20 and therefore stays in soluble form. It can be assumed that the same phenomenon is also observed with other binary systems of an anionic and a non-ionic surfactant. Tween 20 was added according to the molar ratio, which was observed to express good foaming properties. SDS dosages were kept the same so that the results could be compared to the earlier experiments. Therefore, the total amount of surfactant used in the foam generation was much higher than needed to prepare a sheet with good quality. When using the mixture of SDS and

Tween 20, SDS could be dosed less than when used alone. This would result in even lower SDS residues.

In mixed surfactant systems, surfactants form mixed micelles, which are generally composed of all the surfactant species present in the mixture. A mixture of an anionic and a non-ionic surfactant is generally attractive because the incorporation of a non-ionic surfactant in the micelle structure lowers the charge density in the micelle, which increases the entropy of the system. CMC of the mixture of anionic and non-ionic surfactant is lower than of the anionic surfactant. A drastic decrease in CMC compared is observed when non-ionic surfactant increases from 0 to 0.2.[6]

From Figure 37 it can be seen that the measured SDS residues in the sheets made with Tween 20 addition are below the theoretical values. This arises a question if some SDS is left in the fibre network with Tween 20 during the sample preparation as it was also observed that the water extraction of Tween 20 was not that efficient as for SDS (Chapter 8.3).

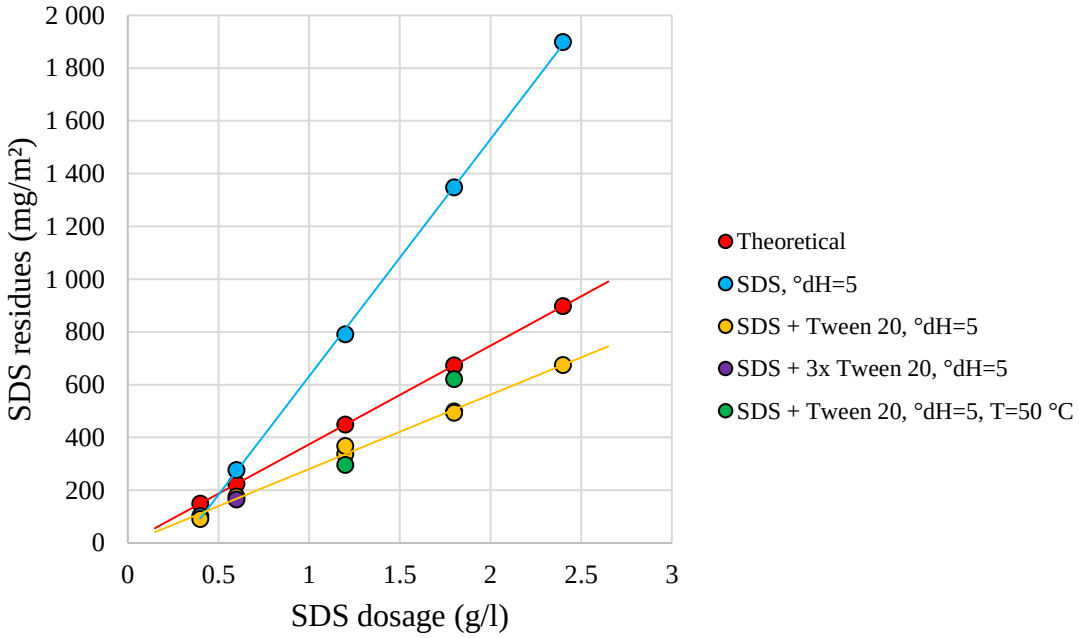


Figure 37. SDS residues when a mixture of SDS and Tween 20 was used in the foam generation. The graph shows measured SDS residues and the corresponding theoretical values (mg/m^2) as a function of SDS dosage (g/l).

Figure 38 shows measured SDS residues in the presence of cationic starch. As can be seen, the measured SDS residues are much higher than the theoretical values and higher than in the conditions without cationic starch. More SDS is left in the fibre network because in addition with the salt formation SDS probably adsorbs on the surface of cationic starch through

electronic interactions. At the dosage of 0.6 g/l, the measured residues are 596 mg/m^2, which is already above the migration limit (500 mg/m^2) set by BfR. In the conditions where water hardness was °dH = 0, the temperature of the suspension was 50 °C or where the surfactant mix was used, SDS dosages up to 1.2 g/l could be used without the measured SDS residues exceeding the migration limit.

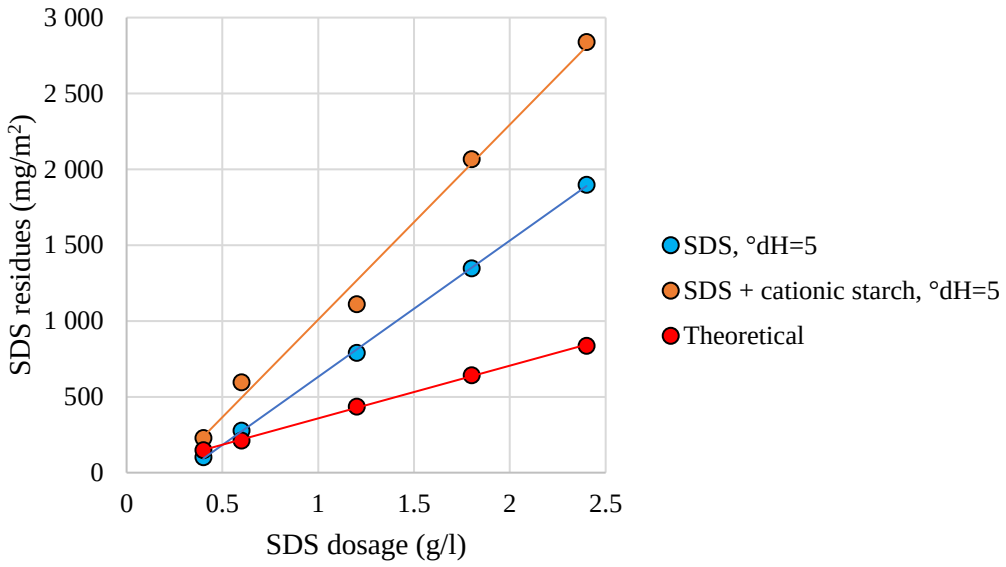


Figure 38. The effect of cationic starch on SDS residues. The graph shows measured SDS residues and the corresponding theoretical values (mg/m^2) as a function of SDS dosage (g/l).

Figure 39 shows an overview from the measurements of SDS residues. The amount of SDS residues is affected by the temperature of foam, water hardness and the presence of other surfactants and cationic additives.

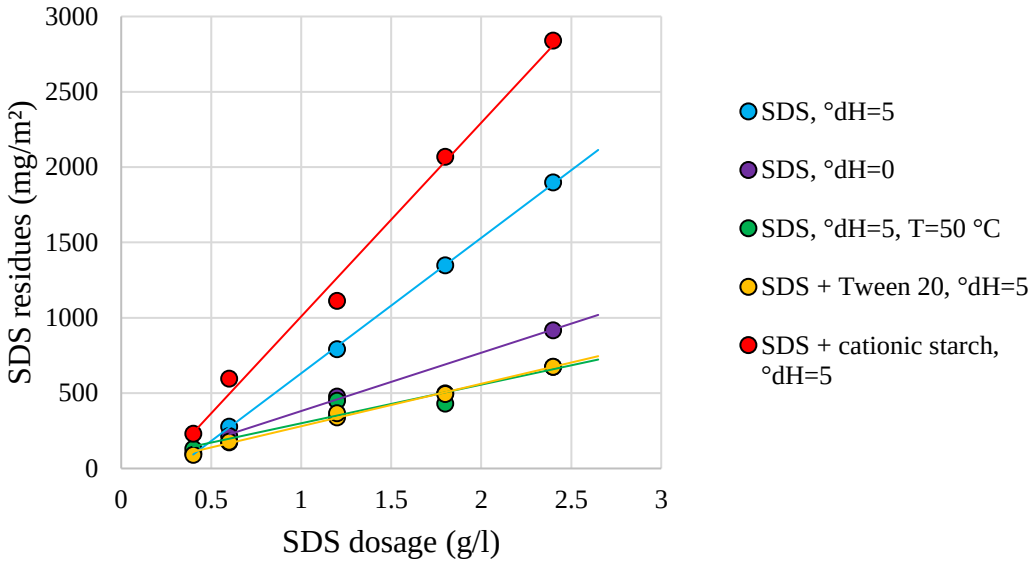


Figure 39. The effect of water hardness, the temperature of the suspension, addition of Tween 20 and addition of cationic starch on the amount of SDS residues. The graph shows measured SDS residues and the corresponding theoretical values (mg/m^2) as a function of SDS dosage (g/l).

8.3 Determination of Tween 20 residues

8.3.1 Calibration of the spectrophotometer

The spectrophotometer was calibrated with Tween 20 standard solutions made in deionised water. Deionised water was used as a blank. Figure 40a and Figure 40b show the calibration curves for LCK333 cuvette test and LCK433 cuvette test, respectively. The calibration of the spectrophotometer succeeded. The calibration curves are linear and the correlation coefficients are ≈ 0.999.

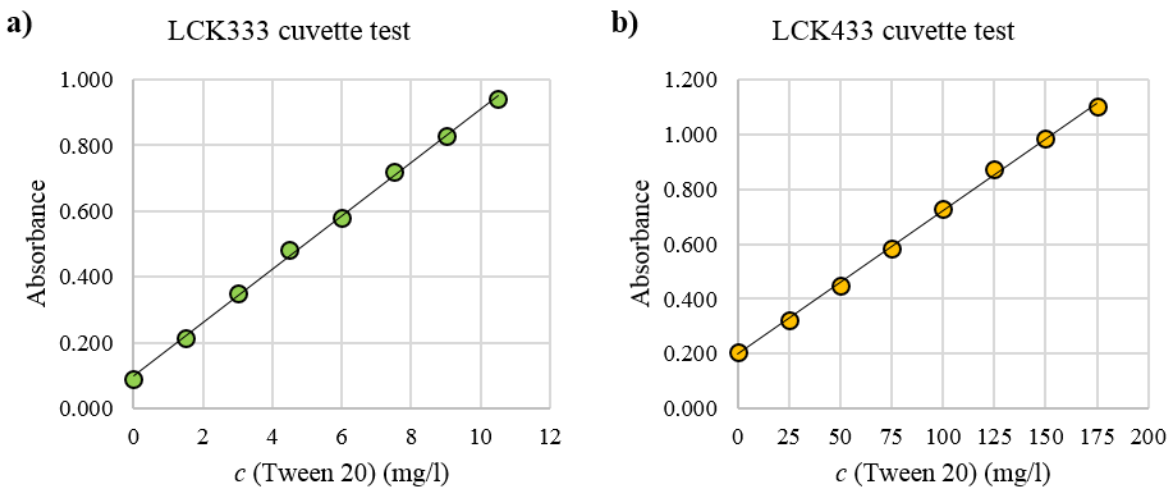


Figure 40. Calibration curves for the spectrophotometric determination of Tween 20. a) The calibration curve for LCK333 cuvette test. The equation of the calibration curve is y = 0.0812x + 0.0996 and the correlation coefficient R^2 = 0.9986. b) The calibration curve for LCK433 cuvette test. The equation of the calibration curve is y = 0.0052x + 0.198 and the correlation coefficient R^2 = 0.9988.

8.3.2 Calibration of HPLC-DAD

For the chromatographic determination of Tween 20, calibrations with pure lauric acid standards and with hydrolysed Tween 20 standard solutions were performed. Figure 41 shows chromatograms for 500 mg/l lauric acid standard solution and hydrolysed 6.67 g/l Tween 20 standard solution. The retention time of lauric acid was approximately 7.18 min. Chromatograms showed symmetric peaks for lauric acid as can be seen from Figure 41.

Figure 42 shows the calibration curve for pure lauric acid. The LOD and LOQ values for pure lauric acid are 60.4 mg/l and 129.7 mg/l, respectively. The hydrolysed Tween 20 standards were prepared in triplicate. Figure 43 shows the calibration curve for Tween 20 obtained from the average peak areas. The initially prepared concentrations, concentrations after hydrolysis and dilution with acetonitrile and the peak areas are tabled in Appendix 6. The LOD and LOQ values for Tween 20 are 0.74 g/l and 2.16 g/l, respectively.

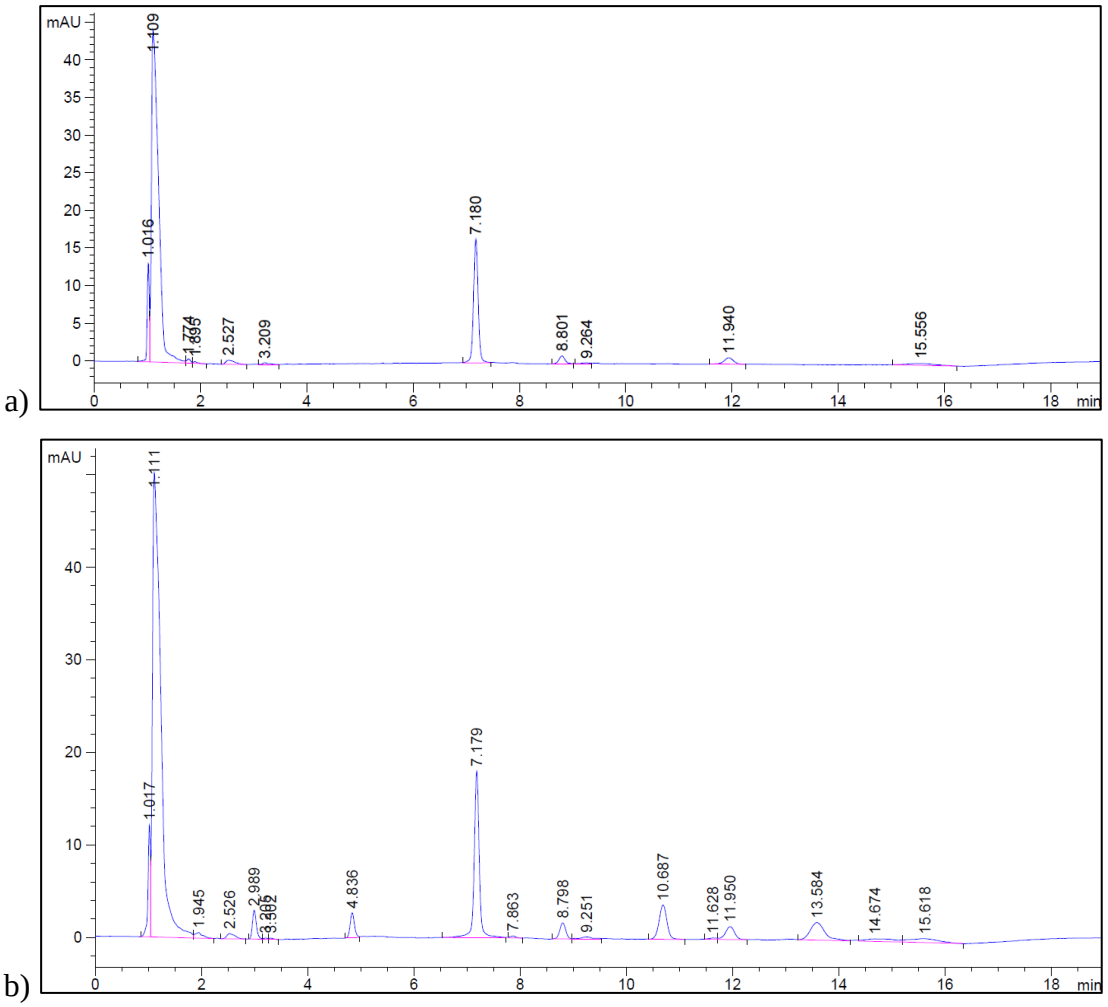


Figure 41. Chromatograms of a) 500 mg/l lauric acid standard solution and b) 6.67 g/l hydrolysed Tween 20 standard solution. Lauric acid is eluted at 7.18 min.

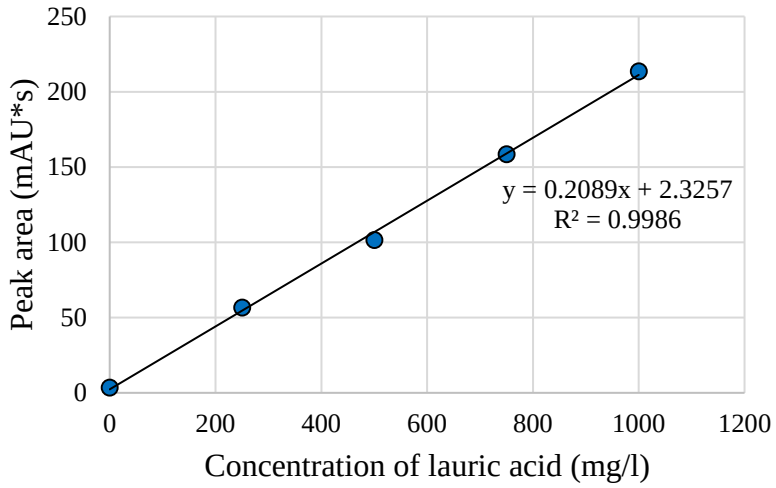


Figure 42. Calibration curve for the chromatographic determination of lauric acid. The graph shows peak area (mAU*s) as a function of concentration (mg/l). The equation of the calibration curve is y = 0.2081x + 2.9466 and the correlation coefficient R^2 = 0.9988.

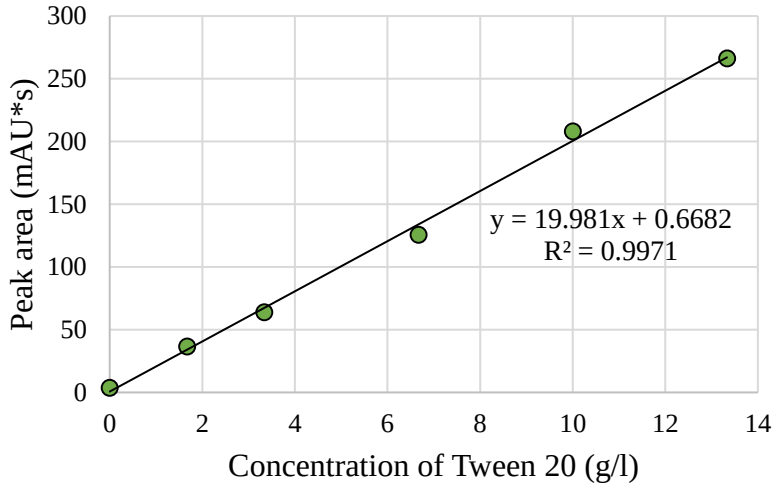


Figure 43. Calibration curve for the chromatographic determination of Tween 20. The graph shows peak area (mAU*s) as a function of concentration (g/l). The equation of the calibration curve is y = 19.887x + 1.6326 and the correlation coefficient R^2 = 0.9973.

The calibration curve of Tween 20 is linear and the correlation coefficient is ≥ 0.99, which indicates that the lauric acid content in Tween 20 is constant. This is the key condition for successful determination of Tween 20 from foam-formed samples. The lauric acid content in Tween 20 as mole percent can be calculated as follows,

$$\text{Lauric acid content (\%)} = \frac{n\ \text{(Lauric acid)}}{n\ \text{(Tween 20)}} \cdot 100\ \% \qquad (15)$$

The concentration of lauric acid was calculated from the peak area using the calibration curve of pure lauric acid. The lauric acid contents in Tween 20 standard solutions were determined using Equation (15). Table 18 shows the calculated lauric acid contents in hydrolysed Tween 20 standard solutions. The lauric acid content varies from 54 to 63 %. The average lauric acid content in Tween 20 was 58 %. This means that 58 % of Tween 20 molecules produce lauric acid as a decomposition product when hydrolysed.

Table 18. The molar lauric acid content in Tween 20 standard solutions.

Standard	*c* (Tween 20)	*n* (Tween 20)	*n* (lauric acid)	Lauric acid content
	g/l	mol	mol	%
Std 1	1.67	8.15E-06	4.82E-06	59
Std 2	3.33	1.63E-05	8.76E-06	54
Std 3	6.67	3.26E-05	1.76E-05	54
Std 4	10.00	4.89E-05	2.95E-05	60
Std 5	13.33	6.52E-05	3.79E-05	58
		Average lauric acid content		58

8.3.3 Comparison of the determination by HPLC-DAD and SES

In the preliminary studies, Tween 20 residues were determined by three different methods. Along with the chromatographic and the colorimetric determination, it was also studied if Tween 20 residues could be determined gravimetrically from the dried Soxhlet extract. This would require that no other substances extracted from the sample. Four different samples were measured.

Lauric acid could be detected from the extracts of the foam-formed samples by HPLC-DAD. However, there were some problems with the chromatographic determination. When measuring the extracts, the lauric acid peak overlapped partially with another unknown peak as can be seen from Figure 44. The overlapping peak was not observed in the hydrolysed Tween 20 standard solutions. It is likely that the peak arises from the presence of residual methanol. One explanation could be acid catalysed esterification reaction. Residual methanol could react with the lauric acid in acidic conditions resulting in an esterified product of lauric acid, i.e. lauric acid methyl ester. Due to the overlapping, the integration of the lauric acid peak is not accurate. In the case of sample 1 (DM = 21.0 %, β = 6 g/l), the peaks merged because the concentration

of lauric acid was so low that the instrument was not able to separate the peaks. Therefore, the integration was done manually by splitting the peaks.

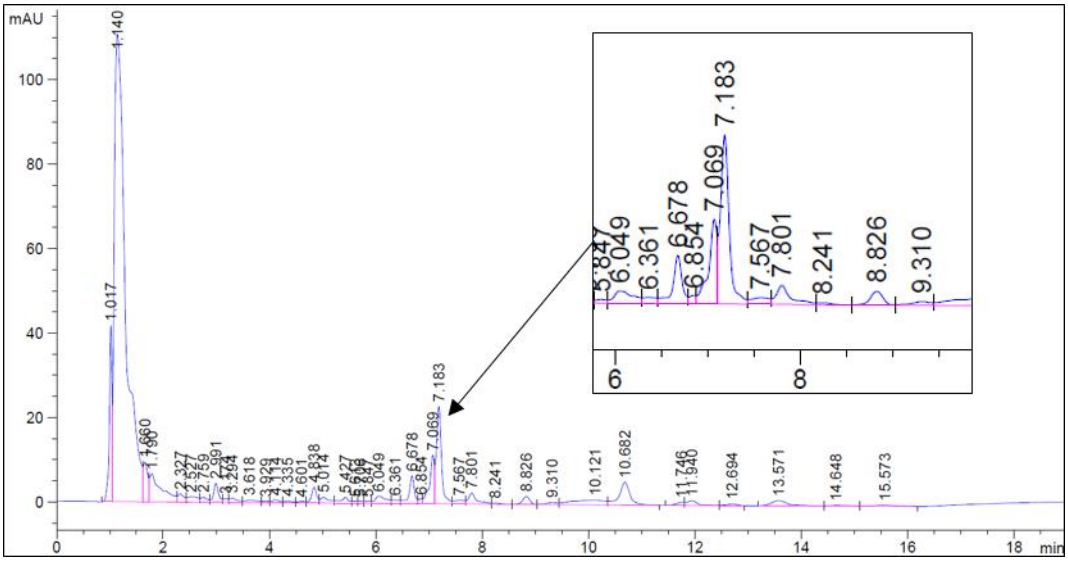


Figure 44. Chromatogram of sample 4 (DM = 5.5 %, β = 12 g/l). Lauric acid is eluted at 7.183 min. Unknown substance is eluted at 7.069 min and the peak overlaps partially with the lauric acid peak.

The peaks were tried to separate from each other by changing the gradient program. The portion of acetonitrile was increased from 60 to 85 %. The gradient program was prolonged so that lauric acid would elute during the gradient phase (i.e. the phase during which the portion of acetonitrile is increasing). The gradient phase was prolonged first from 3.5 min to 10 min and then to 20 min. The overall run times were 23 and 33 min, respectively. However, increasing the portion of acetonitrile and prolonging the gradient phase did not help as the lauric acid peak and the unknown peak merged. Yet another change in the gradient program was tried. The duration of the gradient was kept at 3.5 min during which the portion of acetonitrile was increased from 60 to 85 %. The flow rate was increased from 0.8 ml/min to 1.0 ml/min and the overall run time was reduced to 17 min. Increasing the flow rate decreases the time the molecules spend in the column which should effect on the diffusion of molecules. The more time the molecules spend in the column the more they spread toward lower concentration gradients resulting in broadening of peaks. By increasing the flow rate it was not managed to separate the peaks either. It was decided to use the results obtained by the original gradient program as they correlated well with the results from the gravimetric determination.

LOQ for the determination of Tween 20 was very high, 2.16 g/l. Very high concentrations were measured so the column had a high load. The column pressure remained constant throughout the study. During the studies, a few runs were performed in which the portion of acetonitrile

was increased from 60 to 100 % and kept at 100 % for 5 min. At the end of the run, the high and relatively broad peak was observed. This indicates that a small amount of substances had been left in the column.

Figure 45 shows the measured Tween 20 residues as a diagram. The results are presented in more detail in Appendix 7. The figure shows the theoretical and measured values for each sample in units of mg/g. The theoretical values are calculated from the dry matter content before drying and the dosage of Tween 20. Figure 45 shows that Tween 20 residues increase as the dosage of Tween 20 and the water content of the sample increase. However, the measured Tween 20 residues differ from the theoretical values. The measured Tween 20 residues are close to the theoretical values at the dry matter content level of ~21 %, but at the dry matter content level of ~5.5 % the measured values are significantly lower than the theoretical ones. Table 19 presents results as percentages from the theoretical values. From Table 19 it can be seen that the results obtained by the gravimetric determination are closest to the theoretical values. The results obtained by chromatographic determination show lower percentages compared to the gravimetric determination. This is reasonable as more sample preparation steps are involved in the chromatographic determination.

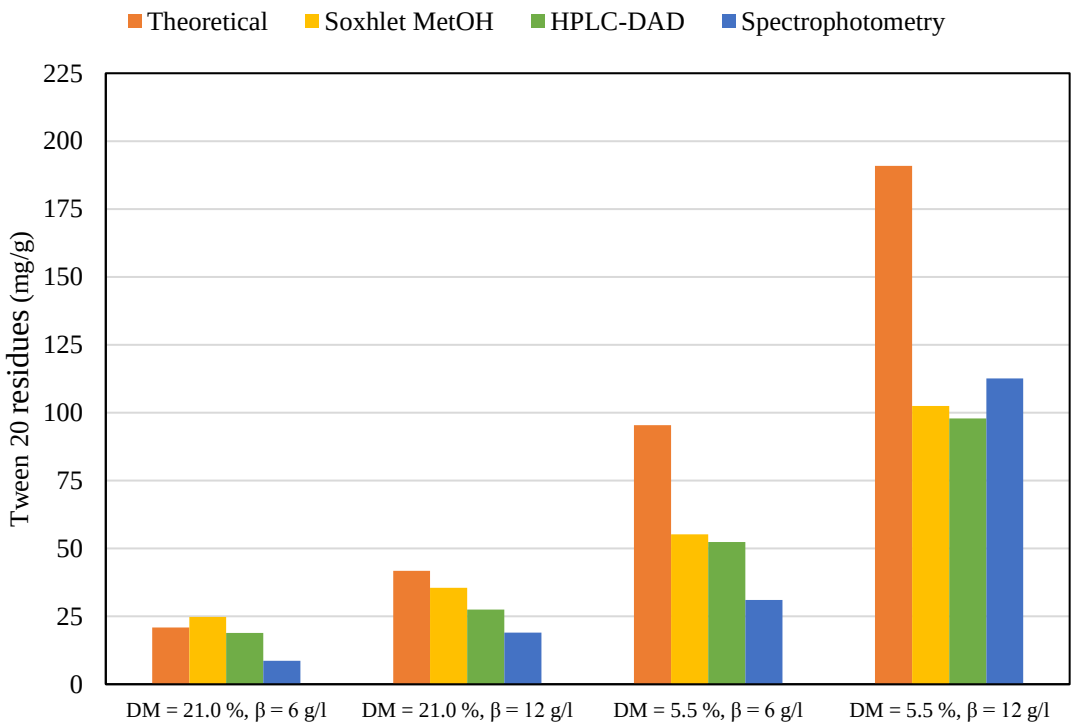


Figure 45. The measured Tween 20 residues (mg/g) in foam-formed samples. The samples are described on the x-axis. DM stands for dry matter content before drying and β for surfactant dosage.

Table 19. Measured Tween 20 residues as percentages from the theoretical values.

Sample	DM	β (g/l)	Percentage (%) from the theoretical value		
			Soxhlet MetOH	HPLC-DAD	Spectrophotometry
1	21.0	6	119	91	41
2	21.0	12	85	66	46
3	5.5	6	58	55	33
4	5.5	12	54	51	59
		Average	79	66	45

The results obtained by the spectrophotometric determination differ most from the theoretical values. In the measurements, LCK433 cuvette tests were used in which the LOQ for Tween 20 was 16.2 mg/l. It was observed that in the spectrophotometric determination, the measured Tween 20 concentrations of samples 1-3 were below LOQ but above LOD. Hence, the results obtained by spectrophotometry are not reliable. A larger amount of the foam-formed sample would have been needed in the determination. On the other hand, sample preparation was challenging due to the high foamability of Tween 20. The suspension produced foam when the sample was disintegrated in water and filtrated.

Another series of six foam-formed samples was measured by spectrophotometry to get quantitative results. LCK333 cuvette tests with lower measuring range were used so there was no need to increase the amount of sample. The measured Tween 20 residues and the corresponding theoretical values are presented in Figure 46. The results are presented in more detail in Table 32 in Appendix 7. The graphs show the same phenomenon as in the preliminary results. The measured Tween 20 residues are lower compared to the theoretical values. At the dry matter content level of 21.0 %, the measured values are approximately 64 % of the theoretical values whereas at the dry matter content level of 5.5. % the measured values are only 35-52 % of the theoretical values. The low recoveries indicate that the water extraction procedure used in the spectrophotometric determination is not suitable for extraction of Tween 20. Tween 20 is probably left in fibre material and filter paper during the filtration.

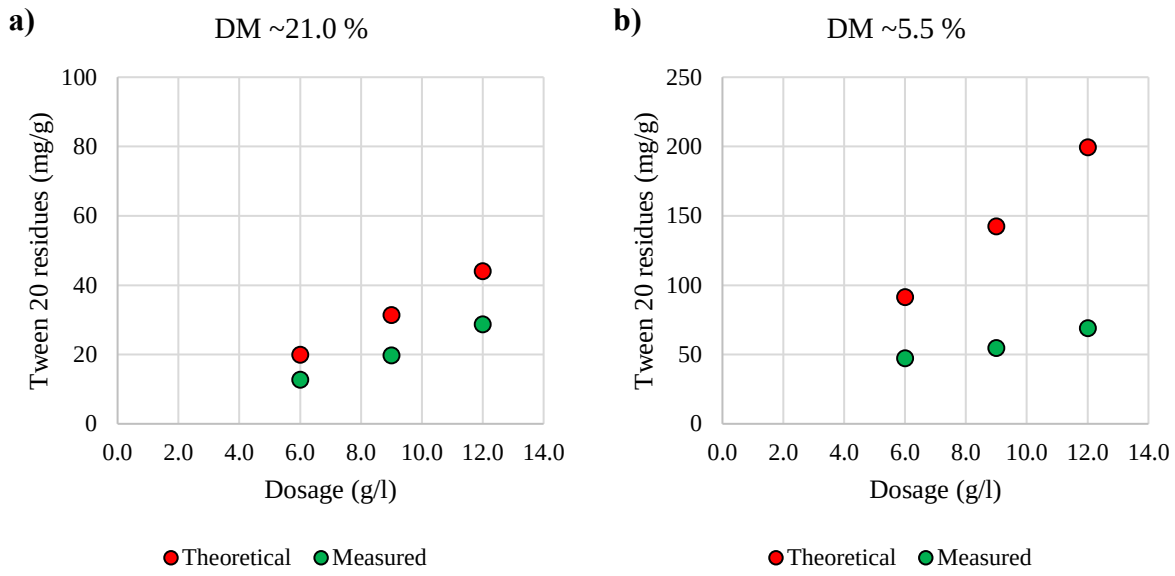


Figure 46. Measured Tween 20 residues (mg/g) by spectrophotometry as a function of Tween 20 dosage (g/l) in samples with dry matter content (DM) of a) 21.0 % and b) 5.5 % before drying.

8.3.4 Comparison of different sample preparation procedures

The effect of sample preparation on the determination of Tween 20 was studied with the sample that was prepared with the Tween 20 dosage of 12 g/l and had the dry matter content of 5.3 % before drying. The sample had the highest Tween 20 content of all the samples studied. It was chosen because it differed the most from the theoretical value. Different sample preparation methods were tested and Tween 20 residues were measured by a spectrophotometer using LCK433 cuvette test.

In the earlier experiments, the fibres were washed with a small amount of deionised water, approximately 100 ml, during the filtration. It was examined if the water extraction of Tween 20 could be enhanced by adding more washing steps in the filtration. Ultrasound-assisted water extraction was also tested. In all the experiments, the amount of sample was approximately 0.3 g and the final volume of the water extract was one litre. Table 20 describes the different sample preparation procedures tested. In the methods 1-3, the sample was disintegrated in 200 ml of deionised water. After the disintegration, the suspension was filtrated through 8 µm ashless filter paper and the fibres were washed with deionised water. The amount of washing water was increased by steps. In the methods 4-5, the sample was not disintegrated but the water was filtered through the dry sample. In the method 4, room-temperature water was used whereas in the method 5, the water was heated to 50 °C. Finally, in the method 6, the sample and 25 ml of

deionised water were placed in 50 ml plastic tube and the sample was sonicated for 3x5min. After sonication the sample was filtered through 8 µm filter paper and washed 3x200 ml of deionised water. In all the methods tested, the obtained filtrates were filtered through 0.45 µm ME membrane before the spectrophotometric measurement.

Table 20. Different water extraction procedures tested for the spectrophotometric determination of Tween 20.

	Description of the water extraction procedures tested
Method 1	1) Disintegration in 200 ml of water 2) Filtration and wash with 1x200 ml of water
Method 2	1) Disintegration in 200 ml of water 2) Filtration and wash with 2x200 ml of water
Method 3	1) Disintegration in 200 ml of water 2) Filtration and wash with 3x200 ml of water
Method 4	Washing with 3x250 ml of deionised water through a dry sample, no disintegration
Method 5	Washing with 3x250 ml of 50 °C deionised water through a dry sample, no disintegration
Method 6	1) Sonication 3x5min in 25 ml of deionised water 2) Filtration and wash with 3x200 ml of water

Figure 47 shows that when the amount of washing water is increased, there is no significant increase in measured Tween 20 residues. The most effective extraction was achieved by using 50 °C water without disintegration. The use of ultrasound did not enhance the water extraction either. The measured residues are still significantly lower than the theoretical values. The percentages from the theoretical values are between 41-57 %.

As the water extraction procedure could not be significantly enhanced, it was studied if more Tween 20 could be extracted by an organic solvent. In the preliminary test, higher results were achieved by Soxhlet extraction with methanol compared to extraction with water used in the spectrophotometric determination. Soxhlet extraction with water, ethanol and acetone were compared. The idea was to study the effect of the continuous flow of solvent and the extraction solvent. These solvents were chosen because they possess different polarities. The order of decreasing polarity is water > ethanol > acetone.

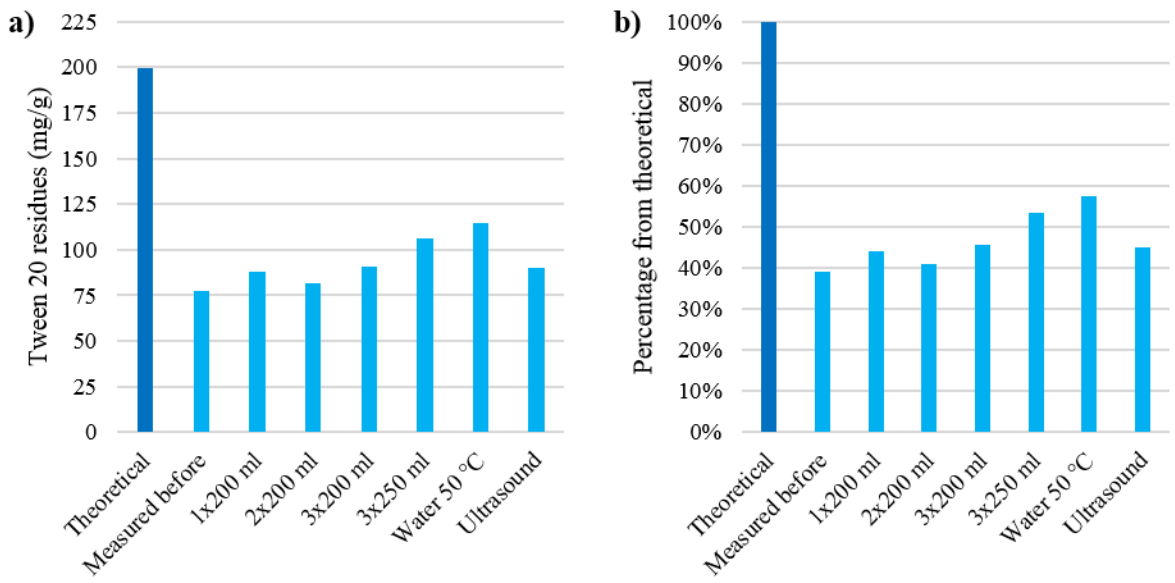


Figure 47. The effect of washing steps, temperature and ultrasound on the water extraction of Tween 20 from foam-formed samples. Measured Tween 20 residues as a) mg/g and b) as a percentage from the theoretical value.

Soxhlet extraction was performed as described earlier but the amount of sample was reduced to 0.3 g and the amount of extraction solvent to 125 ml. Two replicate extractions were made with each solvent. In the case of ethanol and acetone, the solvent was evaporated and the dried extract was weighed. The dried extract was dissolved in deionised water. The water solutions were filtered through 0.45 µm ME membrane before the spectrophotometric determination.

Because Soxhlet extraction is time-consuming (4 h extraction), ultrasound-assisted extraction with ethanol and acetone was also tested to see if the same results could be achieved by more simple extraction. For the ultrasound-assisted extraction 0.3 g of sample and 75 ml of solvent were placed in an Erlenmeyer and the mouth was covered with parafilm. The sample was sonicated for 3x15 min. After sonication, the sample was filtered through 0.45 µm regenerated cellulose (RC) membrane filter. The fibres were washed with 30 ml of solvent. The filtrate was evaporated and the dried extracts were weighed.

Figure 48 shows the results of Soxhlet and ultrasound-assisted extraction experiments. As can be seen, Soxhlet extraction with ethanol and acetone are the most effective for extraction of Tween 20. Results obtained by Soxhlet extraction are higher compared to ultrasound-assisted extraction. More Tween 20 was extracted by ethanol compared to acetone but as the difference is small and only two replicate samples were measured, it cannot be concluded if ethanol would be more effective than acetone. In the previous water extraction tests, the measured Tween 20 residues were as high as 57 % from the theoretical value. It is interesting that in Soxhlet water

extraction the measured Tween 20 residues are only 39 %. The continuous flow of water in an elevated temperature does not enhance the extraction of Tween 20. The lower measured residues may be due to hydrolysis of Tween 20 as the hydrolysis is accelerated by increased temperature. Another explanation may be that Tween 20 is left in the cellulose extraction thimble used in Soxhlet extraction.

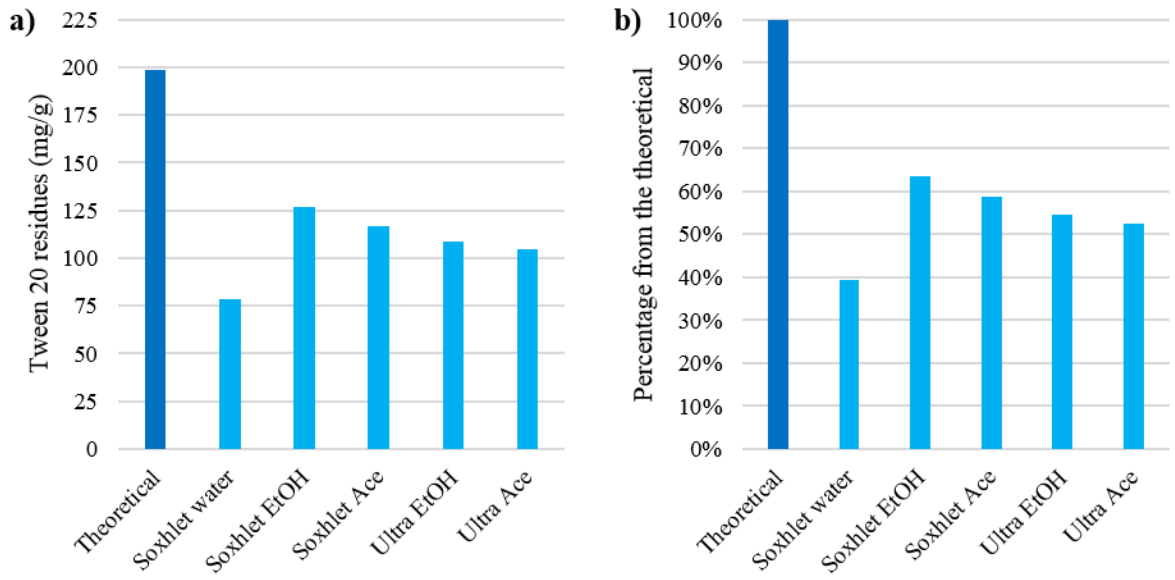


Figure 48. Comparison of Soxhlet and ultrasound-assisted extraction for the extraction of Tween 20 from foam-formed samples. Measured Tween 20 residues as a) mg/g and b) as a percentage from the theoretical value. The abbreviations EtOH and Ace mean ethanol and acetone.

The measured Tween 20 residues were not close to the theoretical values even if organic solvents were used as extraction solvents. This raises the question if there is actually fewer Tween 20 in the sample than theoretically estimated. The sample chosen in the sample preparation studies was very wet (DM content before drying 5.3 %), the dosage of Tween 20 was high (12 g/l) and the sample was dried in an oven. Non-ionic surfactants are capable of reducing surface tension at lower concentrations compared to anionic surfactants. It is possible that due to the low surface tension, water has drained during the oven drying which would result in lower amount surfactant residues as the surfactant is lost within the water.

The results from the determination of Tween 20 residues show that Tween 20 does not behave like SDS in the fibre network. The fact that all the measured residues are lower than the theoretical values indicates that Tween 20 is not left in the fibre network more than theoretically estimated. However, when water is used as an extraction solvent, Tween 20 may be left in fibres and filter papers during filtration. Tween 20 is more easily removed from the fibre network by

an organic solvent compared to water. Foaming of Tween 20 water solution makes the extraction difficult. When an organic solvent is used, Tween 20 does not produce foam.

8.4 Interferences in the determination by SES

As mentioned earlier (in Chapter 4.2.2), other surfactants may cause interference in the determination of surfactants by SES. Because the mixture of SDS and Tween 20 was used in this study, the effect of the other surfactant on the spectrophotometric determination was studied. The effect of SDS on the determination of Tween 20 was studied by measuring the same Tween 20 concentration (6.0 mg/l) without SDS and at three different concentrations of SDS (0.5, 2.0 and 20 mg/l). LCK333 cuvette tests were used in the determination of Tween 20. Respectively, the same SDS concentration (1.0 mg/l) was measured without Tween 20 and at three different Tween 20 concentrations (1.0, 5.0 and 10 mg/l).

Figure 49 shows that the presence of Tween 20 does not affect the spectrophotometric determination of SDS when the Tween 20 concentration is up to 10 mg/l. A slight increase in the measured SDS concentration was observed when the Tween 20 concentration was 10 mg/l but the increase is only 8.9 % when compared to the sample that did not contain any Tween 20. The difference is so small that it can be included in the dilution error.

On the other hand, the spectrophotometric determination of Tween 20 is affected by the presence of SDS. At SDS concentrations of 0.5 mg/l and 2.0 mg/l, no interference is observed but at SDS concentration of 20 mg/l, there is 61 % decrease in the measured Tween 20 concentration. SDS causes negative interference because it is anionic and replaces the anionic dye molecule in the complex. SDS forms a complex with Tween 20 and large cations that is colourless so it does not absorb at the measuring wavelength. Therefore, we can conclude that the presence of any anionic surfactant in high concentrations (>> 2.0 mg/l) causes negative interference on the spectrophotometric determination of any non-ionic surfactant. The interference could be overcome by removing the anionic surfactant from the sample for example by SPE using anion exchange sorbent. If the concentration of SDS is known and it is constant, so-called matrix matching could also be used which means that the calibration solutions contain the same amount of anionic surfactant as the sample.

Anti-foaming agents are used to eliminate or control foaming in industrial wastewater treatment. Anti-foaming agents include e.g. insoluble oils, silicones, alcohols, stearates and glycols.[112] They act in different ways but the principle is the same: anti-foaming agents disrupt

the assembly of surfactants at the bubble surface causing bubble coalescence.[1] Silicone structure is composed of Si-O-Si backbone so it contains ether bridges similarly like non-ionic surfactants. As there may be a structural similarity between anti-foaming agents and non-ionic surfactants, it was studied if the presence of anti-foaming agent causes interference in the spectrophotometric determination of non-ionic surfactants.

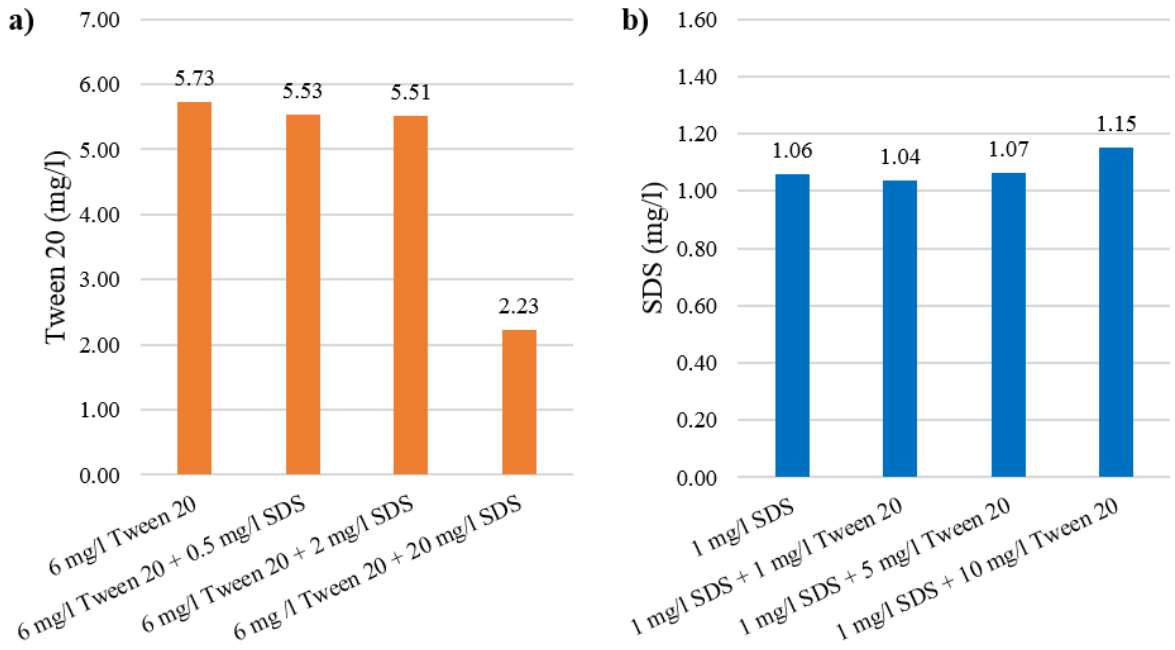


Figure 49. a) The effect of SDS addition on the spectrophotometric determination of Tween 20. b) The effect of Tween 20 addition of the spectrophotometric determination of SDS.

The effect of the anti-foaming agent was studied by measuring two different concentrations of Tween 20, 1.0 and 10 g/l, without an anti-foaming agent, at antifoam concentration of 600 µl/l and antifoam concentration of 1 200 µl/l. Table 21 shows an overview from the prepared samples. The samples were diluted to the measuring range and measured with LCK433 cuvette test.

Table 21. The samples used to study the effect of the antifoaming agent on the spectrophotometric determination of Tween 20.

Sample	Dilution coeff.	Concentration after dilution	
		Tween 20 (mg/l)	Antifoam (µl/l)
1 g/l Tween 20	10	100	0
1 g/l Tween 20 + 600 µl/l antifoam	10	100	60
1 g/l Tween 20 + 1200 µl/l antifoam	10	100	120
10 g/l Tween 20	100	1 000	0
10 g/l Tween 20 + 600 µl/l antifoam	100	1 000	6
10 g/l Tween 20 + 1200 µl/l antifoam	100	1 000	12

Figure 50 shows the results from the measurements. It can be seen that no interference caused by the anti-foaming agent is observed at the Tween 20 concentration of 10 g/l. There, the antifoam concentration after dilution to the measuring range was either 6 or 12 µl/l. When Tween 20 concentration of 1 g/l was measured, a lower dilution factor was used when the amount of antifoam was higher. The sample which contained 600 µl/l antifoam does not show a significant increase in measured Tween 20 concentration but the sample which had twice as high antifoam concentration, 1 200 µl/l, shows 21 % increase in measured Tween 20 concentration compared to the sample made in pure deionised water. There, the antifoam concentration after dilution was 120 µl/l. It seems that the anti-foaming agent used in these tests has some capability to interact with the anionic dye in solvent extraction spectrophotometry.

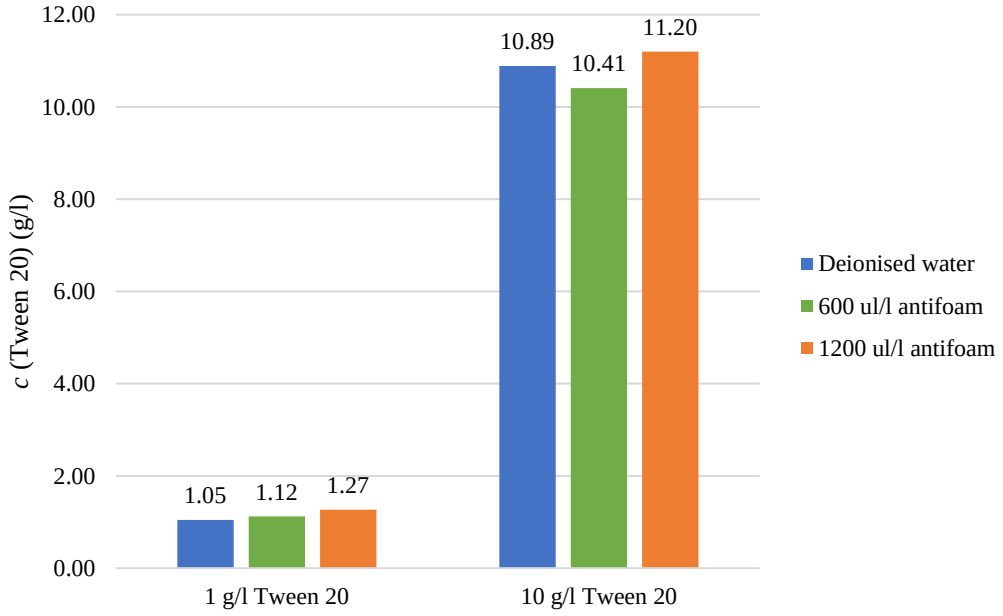


Figure 50. The effect of the antifoaming agent on the spectrophotometric determination of Tween 20.

To verify this conclusion, antifoam solutions without Tween 20 were also determined by spectrophotometry. Concentrations of 6, 60 and 600 µl/l were measured using LCK433 cuvette test. Table 22 shows the measured absorbances for antifoam water solutions. Antifoam concentrations 6 and 60 µl/l gave an absorbance below the LOQ, so it can be concluded that those concentrations do not affect on the measurement. However, antifoam concentration of 600 µl/l gave an absorbance of 0.643, which indicates that the used antifoam clearly causes interference when the concentration is sufficiently high. The organic phase was clear and coloured, so the interference is not caused by light scattering or absorption of antifoamer itself. Clearly, the antifoaming agent can interact with the anionic ion-pair reagent.

Table 22. Antifoam solutions measured by spectrophotometry using LCK433 test.

c (antifoam) (µl/l)	Absorbance
6	0.229
60	0.257
600	0.643

8.5 Determination of 4-DBSA

Standard solutions of 4-DBSA were diluted from 10 g/l stock solution in deionised water. The applicable measurement area was searched by wavelength scan measurements. Wavelength scan measurements were conducted from 350 to 190 nm. Two absorbance maximums were observed, which is in accordance with the literature.[3] The program of the instrument was used to calculate the absorbance maximums from the spectra. The spectra drawn by the instrument showing the absorbance maximums are presented in Appendix 8. From all the spectra, the mean value was calculated for the absorbance maximum. The absorbance maximums were 194 nm and 224 nm. Figure 51 and Figure 52 show the spectra from the wavelength scan measurements. It can be seen that 4-DBSA absorbs more strongly at the wavelength of 194 nm compared to 224 nm, i.e. lower concentrations can be detected at 194 nm. The suitable measuring range is 1-6 mg/l for the wavelength of 194 nm and 5-25 mg/l for the wavelength of 224 nm.

Absorbance measurements at 194 nm and at 224 nm were performed with the suitable concentrations and calibration curves were established. Reference measurements were performed by Hitachi U-2900. Results from the absorbance measurements are presented in Appendix 8. In PerkinElmer, the measurements were performed with a reference cell that contained deionised water. In the measurements performed by Hitachi, there was no reference

cell so the absorption of water and quartz cuvette are included in the absorbance values and therefore the absorbance values are higher than measured by PerkinElmer.

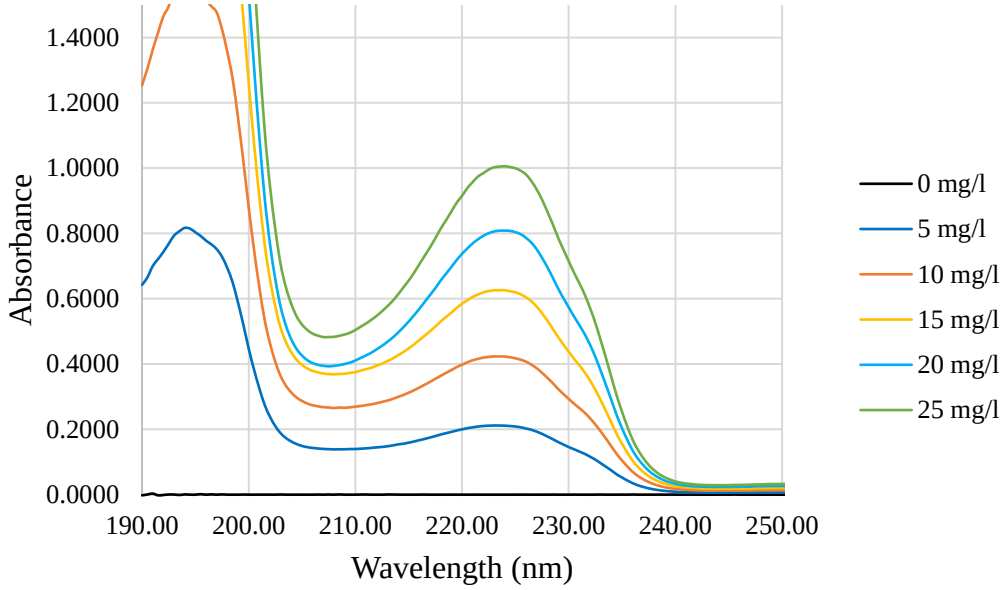


Figure 51. The spectra of 4-dodecylbenzenesulphonic acid for concentrations of 0, 5, 10, 15, 20 and 25 mg/l. The concentrations are suitable for determination at 224 nm.

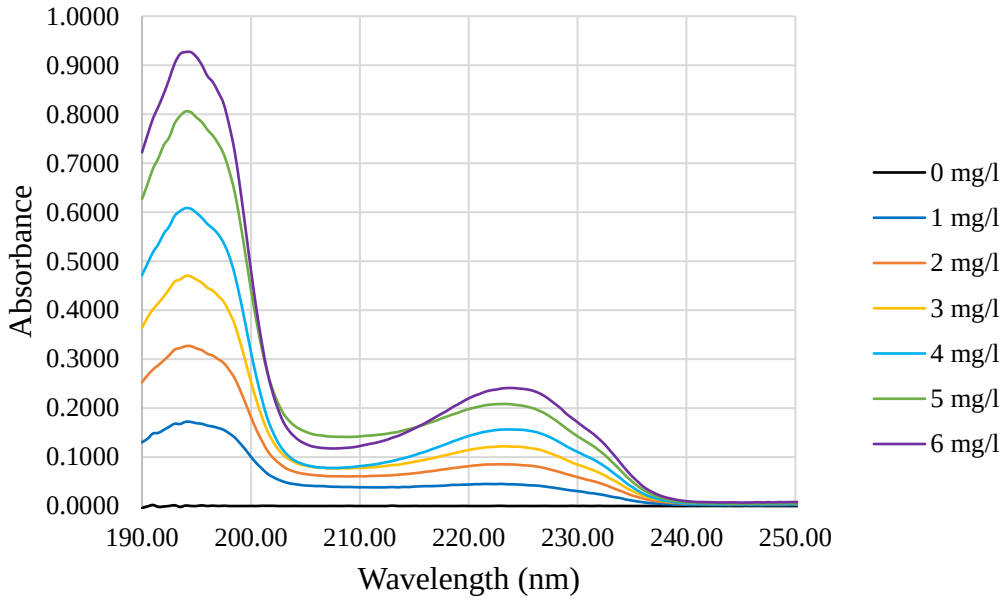


Figure 52. The spectra of 4-DBSA for concentrations of 0, 1, 2, 3, 4, 5 and 6 mg/l. The measuring range is suitable for determination at 194 nm.

Figure 53 shows the calibration curves obtained by PerkinElmer and Figure 54 shows the calibration curves obtained from the reference measurements performed with Hitachi. Good

correlation could be obtained at both wavelengths. The wavelength of 224 nm is slightly more accurate as the correlation coefficient is ≥ 0.999. The two spectrophotometers show a similar response to concentration as the slopes of the calibration curves are almost similar.

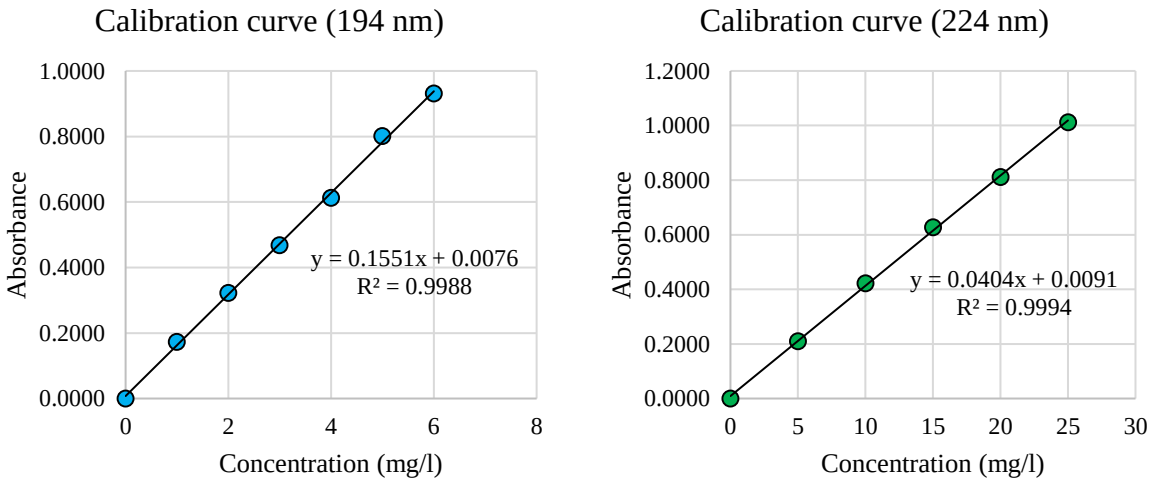


Figure 53. Calibration curves for the determination of 4-DBSA by direct UV absorption at two different wavelengths. The measurements were performed with PerkinElmer Lambda 25.

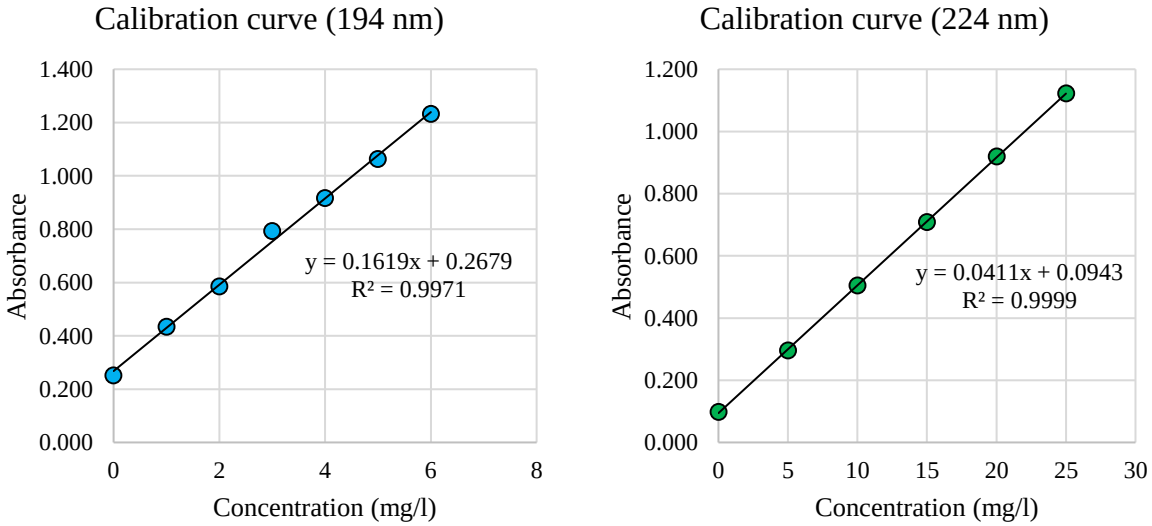


Figure 54. Calibration curves for the determination of 4-DBSA by direct UV absorption at the wavelength of 194 nm. The measurements were performed with Hitachi U-2900.

The molar absorptivity can be calculated using Equation (9). The molar absorptivity values of 4-DBSA at wavelengths of 194 nm and 224 nm were calculated from the absorbance measurements performed with PerkinElmer instrument. The mean values for molar absorptivity

at 194 nm and at 224 nm were 52 179 M^{-1} cm^{-1} and 13 531 M^{-1} cm^{-1}, respectively. The molar absorptivity of 4-DBSA is almost four times higher at 194 nm compared to 224 nm.

LOD and LOQ values for the determination of 4-DBSA are presented in Table 23. It can be seen that LOQs are low. By Hitachi LOQs were below 1 mg/l at both measuring wavelengths. The lowest LOQ was 0.51 mg/l. LOQ at 224 nm for the determination by PerkinElmer is 1.61 mg/l whereas for the determination by Hitachi it is only 0.67 mg/l.

Table 23. LOD and LOQ for the determination of 4-DBSA. The table shows LOD and LOQ as absorbances and as concentrations (mg/l).

Spectrophotometer	Wavelength (nm)	LOD		LOQ	
		A	*c* (mg/l)	*A*	*c* (mg/l)
PerkinElmer Lambda 25	194	0.0258	0.12	0.0862	0.51
	224	0.0223	0.33	0.0742	1.61
Hitachi U-2900	194	0.294	0.16	0.393	0.77
	224	0.105	0.26	0.122	0.67

9 CONCLUSIONS

The determination of three different surfactants was studied: SDS, Tween 20 and 4-DBSA. Methods for the determination of SDS and Tween 20 residues from solid foam-formed samples were developed. Surfactant residues were determined from foam-formed hand sheets made in the laboratory. SDS residues were determined by ICP-OES and solvent extraction spectrophotometry (SES). For the determination by ICP-OES, ultrasound-assisted nitric acid digestion was performed. For the determination by SES, a new sample preparation method was used in which the sample was disintegrated in water and the suspension was filtered, i.e. SDS was extracted in water. Tween 20 residues were determined by HPLC-DAD and SES. For the chromatographic determination, Tween 20 was extracted in methanol using Soxhlet extraction procedure. For the determination by SES, similar water extraction set up was used as in the case of SDS. In addition to analysis of surfactant residues, determination of 4-DBSA in water solution by direct UV absorption was studied.

As expected, it was observed that surfactant residues increased as the surfactant dosage and the water content of the sample before drying increased. Drying method had a significant influence on the results. In the case of SDS, air drying and rapid drying of the prepared sheets was compared and it was observed that rapid drying resulted in the lower amount of SDS residues because SDS was moved into suction boards. Therefore, it is recommended that the determination of grammage and surfactant residues are performed from separate samples.

The determination of SDS residues succeeded. ICP-OES and SES gave very similar results, which indicates that water can be used as the extraction solvent for SDS. SES is based on detection of SDS molecule. As the determination of SDS by SES succeeded, it can be concluded that SDS does not degrade in the foam-formed sample and it remains surface active.

When water hardness was °dH = 5, the measured SDS residues were higher than the theoretical values estimated from the dry matter content before drying and the SDS dosage. The measured SDS residues were approximately triple compared to the corresponding theoretical values. However, when the water hardness was °dH = 0, the measured SDS residues were equal to the theoretical residues. Similarly, SDS residues decreased to the theoretical level when the water temperature was raised from room temperature to 50 °C or when Tween 20 was added with SDS. It can be concluded that SDS forms an insoluble salt with calcium and magnesium ions, which is left in the product and therefore SDS residues increase. When the temperature is raised, the solubility of the salt increases and SDS remains in soluble form. Addition of non-ionic surfactant results in the formation of mixed micelles. SDS is bound in the micelle structures and therefore stays in soluble form. Addition of cationic starch with water hardness of °dH = 5 resulted in even more higher SDS residues. This is probably due to the attractive electronic interactions between the cationic starch and anionic SDS.

Tween 20 could be detected by both HPLC-DAD and SES. HPLC-DAD gave higher results compared to the determination by SES. The measured Tween 20 residues were close to the theoretical values in the air-dried samples (DM before drying ~21 %) but in the bulky samples dried in an oven (DM before drying ~ 5.5 %), the measured Tween 20 residues were only about half of the theoretical values. It is possible that the drainage continued during the oven drying due to the low surface tension resulting in the loss of Tween 20. On the other hand, it was also observed that Tween 20 is not fully extracted from the fibre network by water. When different extraction procedures were compared, it was discovered that the water extraction procedure could be enhanced to some extent by increasing the amount of water in washing the fibres. Comparison of Soxhlet extraction with water, ethanol and acetone showed clearly that more

Tween 20 was extracted by ethanol and acetone than water. In Soxhlet extraction, cellulose extraction thimbles are used, so there were additional fibres in the extraction. It seems that Tween 20 interacts with fibres more strongly than SDS. Tween 20 is extracted from the fibre network more efficiently by an organic solvent.

The effect of another surfactant on the determination by SES was studied. Tween 20 was not observed to cause any interference in the determination of SDS. However, the presence of SDS causes negative interference in the determination of Tween 20. No interference was observed at concentrations of 0.5 and 2.0 mg/l of SDS but when the concentration of SDS was 20 mg/l, there was a 61 % in the measured Tween 20 concentration. This is because SDS replaces the anionic dye and a colourless complex with Tween 20 is formed.

Determination of 4-DBSA in water solution by direct UV-absorption succeeded. The absorbance maximums for 4-DBSA were observed at 194 nm and 224 nm. Calibration curves for both wavelengths were established. By using the wavelength of 224 nm, excellent correlation is achieved ($R^2 \geq 0.999$). Accuracy at the wavelength of 194 nm is a bit poorer ($R^2 \geq 0.99$) but it is more sensitive wavelength. At the wavelength of 194 nm, concentrations of 1.0-6.0 mg/l can be determined whereas the wavelength of 224 nm is suitable for the measuring range of 5.0-25.0 mg/l.

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APPENDIXES

Appendix 1. GHS hazard classes and pictograms

Table 24. Hazard classes defined in GHS.[60]

Hazard classes in GHS	
Physical hazards	Explosives
	Flammable gases
	Aerosols
	Oxidising gases
	Gas under pressure
	Flammable liquids
	Flammable solids
	Self-reactive substances and mixtures
	Pyrophoric liquids
	Pyrophoric solids
	Self-heating substances and mixtures
	Substances and mixtures which, in contact with water, emit flammable gases
	Oxidising liquids
	Oxidising solids
	Organic peroxides
	Corrosive to metals
	Desensitised explosives
Health hazards	Acute toxicity
	Skin corrosion/irritation
	Serious eye damage/eye irritation
	Respiratory or skin sensitisation
	Germ cell mutagenicity
	Carcinogenicity
	Reproductive toxicity
	Specific target organ toxicity - Single exposure
	Specific target organ toxicity - Repeated exposure
	Aspiration hazard
Environmental hazards	Hazardous to the aquatic environment
	Hazardous to the ozone layer

Table 25. Hazard pictograms and their meanings.[60]

Code	Hazard pictogram	Meaning
GHS01		Explosive
GHS02		Flammable
GHS03		Oxidising
GHS04		Gas under pressure
GHS05		Corrosive
GHS06		Acute toxicity
GHS07		Harmful, skin and eye irritation, respiratory irritation, hazardous to ozone layer
GHS08		Health hazard
GHS09		Toxic to aquatic environment

Appendix 2. Theoretical surfactant residues

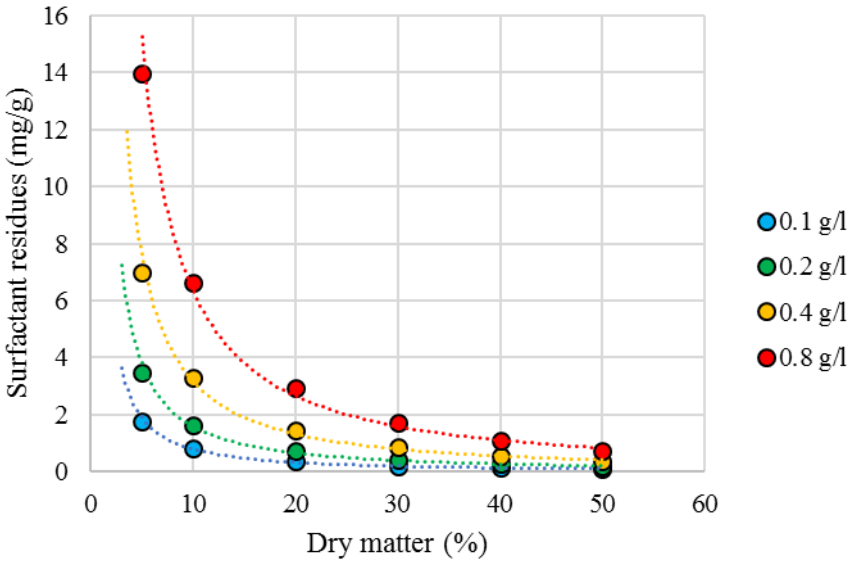

Figure 55. Theoretical residues of an anionic surfactant as a function of dry matter content at different dosage levels. The graph shows dry matter content (%) on the x-axis and surfactant residues (mg/g) on the y-axis.

Appendix 3. ICP-OES measurements

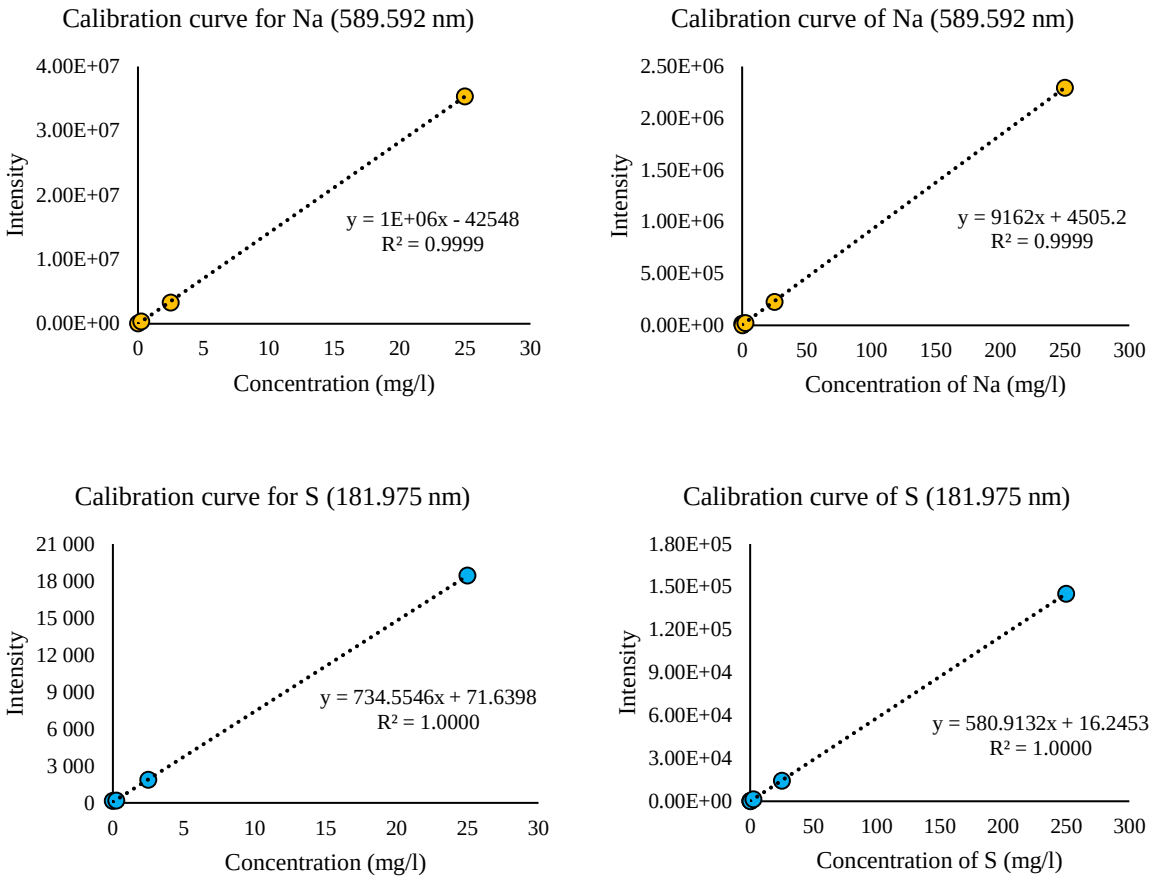

Figure 56. Calibration curve of Na (589.592 nm) and S (181.975 nm). In the left, concentrations of standards are 0.25, 2.5 and 25 mg/l. In the right, concentrations of standards are 0.25, 2.5, 25 and 250 mg/l. The graph shows concentration (mg/l) on the x-axis and intensity on the y-axis.

Table 26. The results of ICP-OES measurements. The table shows SDS dosage (β), the measured concentrations of Na and S, Na and S contents in the solid sample and the amount of SDS residues calculated from Na and S contents.

Sample code	Drying	β (SDS)	Na		S (180.669 nm)		SDS from Na	SDS from S*
		g/l	mg/l	mg/g	mg/l	mg/g	mg/m^2	mg/m^2
Blank		0	0.614	0.059	0.737	0.071	-	-
1	Air drying	0.4	2.188	0.216	2.329	0.230	196	143
2		0.6	4.038	0.403	3.136	0.313	431	217
3		1.2	6.583	0.599	8.227	0.748	677	609
4		2.4	12.601	1.159	20.154	1.853	1379	1603
10.1		1.2	9.356	0.902	10.555	1.018	1058	852
10.2		1.2	9.213	0.900	10.561	1.032	1055	864
11.1		1.8	10.812	1.075	18.466	1.836	1275	1588
11.2		1.8	10.721	1.033	18.570	1.789	1221	1545
12.1		2.4	12.546	1.256	23.324	2.334	1501	2036
12.2		2.4	11.986	1.191	25.428	2.528	1420	2210
5	Rapid drying	0.4	1.237	0.121	0.989	0.096	77	23
6		0.6	1.498	0.145	0.849	0.082	108	10
7		1.2	3.071	0.299	1.571	0.153	301	74
8		2.4	6.537	0.616	9.506	0.896	699	742
13.1		1.2	3.823	0.375	1.723	0.169	396	88
13.2		1.2	3.909	0.380	1.677	0.163	403	83
14.1		1.8	4.432	0.441	1.481	0.147	479	69
14.2		1.8	4.428	0.435	2.092	0.205	471	121
15.1		2.4	5.600	0.545	5.250	0.511	609	395
15.2		2.4	4.856	0.479	2.054	0.203	527	118
16	Oven drying	0.4	5.404	0.529	27.908	2.731	589	2393
17		0.6	6.773	0.677	46.292	4.626	775	4098
18		1.2	9.656	0.980	67.329	6.830	1154	6080
19		1.8	14.175	1.408	95.133	9.447	1692	8435
20		2.4	18.528	1.824	82.118	8.082	2213	7207

*The wavelength 180,669 nm was used in the calculations because of its higher intensities.

Appendix 4. Determination of SDS residues by solvent extraction spectrophotometry

Table 27. The results from the spectrophotometric determination of SDS residues. The table shows SDS dosage (β), the amount of sample, dilution factor, absorbance, the measured SDS concentrations and SDS residues in units of mg/g and mg/m^2.

Sample code	Drying	β (SDS) g/l	*m* g	Dilution	*A*	*c* (SDS) mg/l	SDS mg/g	SDS mg/m^2
1	Air drying	0.40	1.0461	1	0.497	1.218	1.164	116
2		0.60	1.0527	1	0.916	2.446	2.323	232
3		1.20	1.0040	5	0.473	1.147	5.713	571
4		2.40	1.0261	10	0.68	1.754	17.094	1709
10.1		1.20	0.5079	5	0.362	0.822	8.090	809
10.2		1.20	0.5175	5	0.382	0.880	8.506	851
11.1		1.80	0.5089	10	0.385	0.889	17.473	1747
11.2		1.80	0.5161	10	0.388	0.898	17.399	1740
12.1		2.40	0.5060	10	0.47	1.138	22.498	2250
12.2		2.40	0.5303	10	0.493	1.206	22.738	2274
5	Rapid drying	0.40	1.0291	1	0.184	0.300	0.291	29
6		0.60	1.0139	1	0.319	0.696	0.686	69
7		1.20	1.0451	1	0.726	1.889	1.807	181
8		2.40	1.0272	5	0.443	1.059	5.156	516
13.1		1.20	1.0079	5	0.196	0.335	1.662	166
13.2		1.20	1.0272	5	0.177	0.279	1.360	136
14.1		1.80	0.5026	1	0.472	1.144	2.277	228
14.2		1.80	0.5204	1	0.594	1.502	2.886	289
15.1		2.40	0.5245	1	1.028	2.774	5.289	529
15.2		2.40	0.5038	1	0.607	1.540	3.057	306
16	Oven drying	0.40	0.5219	10	0.552	1.379	26.418	2642
17		0.60	0.5218	10	0.953	2.554	48.953	4895
18		1.20	0.5069	20	0.651	1.669	65.852	6585
19		1.80	0.5071	50	0.443	1.059	104.439	10444
20		2.40	0.1286	50	0.158	0.224	86.970	8697
20		2.40	0.1286	10	0.448	1.074	83.505	8351
20		2.40	0.5083	50	0.335	0.743	73.047	7305

Appendix 5. Measured SDS residues presented in units of mg/g

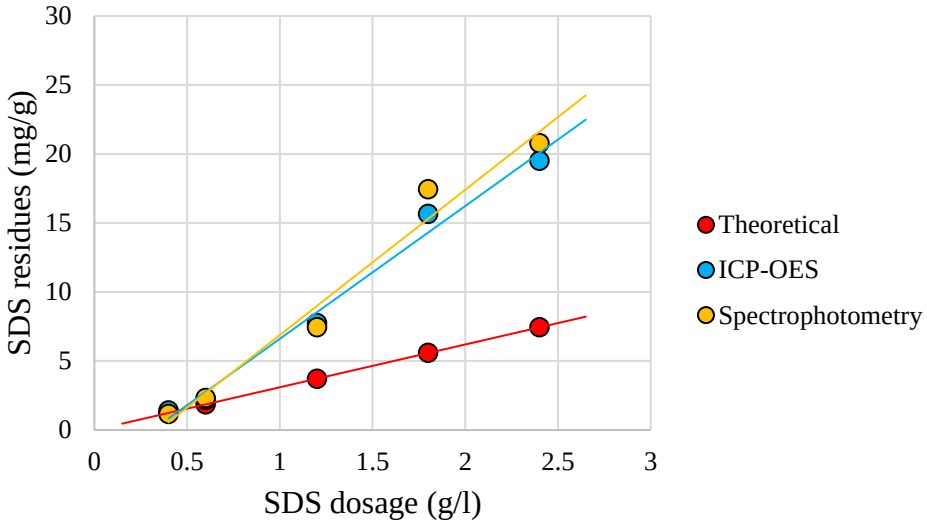

Figure 57. SDS residues in foam-formed hand sheets made by vacuum and dried at air. Some of the data points are average values of replicate samples. At the dosage of 0.6 g/l SDS residues are 2.32 mg/g by spectrophotometric determination. When one gram of sample is disintegrated into one litre of water, SDS concentration of the water solution is 2.32 mg/l (2.32 ppm).

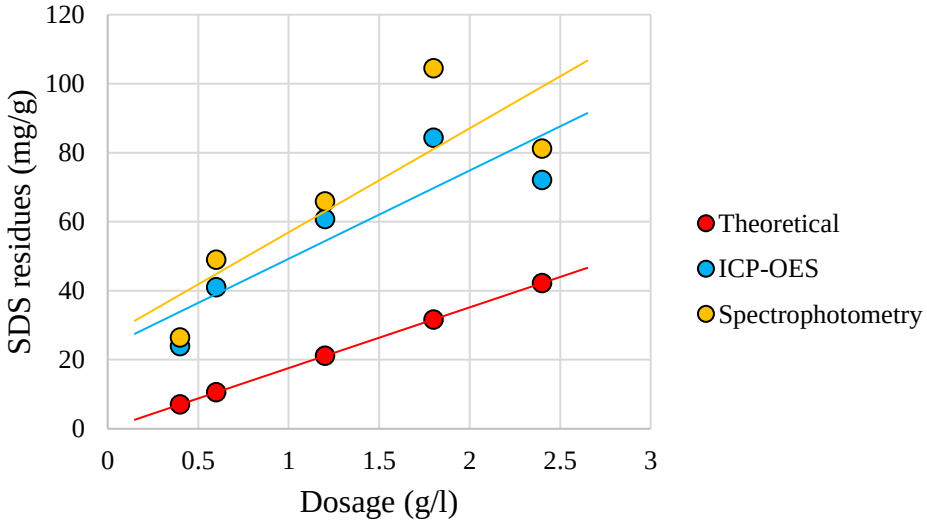

Figure 58. SDS residues in foam-formed hand sheets made without vacuum and dried in an oven at 70 °C. Some of the data points are average values of replicate samples. At the dosage of 1.8 g/l SDS residues are 104.4 mg/g by spectrophotometric determination. When one gram of sample is disintegrated into one litre of water, SDS concentration of the water solution is 104.4 mg/l (104.4 ppm).

Appendix 6. The calibration of HPLC-DAD

Table 28. The concentrations of hydrolysed Tween 20 standard solutions (mg/l) and the corresponding peak area values (mAU*s). The table shows the initial prepared concentrations, concentrations after 6x dilution (1 ml of standard solution + 1 ml of 4 M H_2SO_4 + 4 ml of acetonitrile) and the average peaks areas obtained from three replicate measurements.

	Tween 20 g/l	Tween 20 (after 6x dilution) g/l	Average peak area mAU*s
Blank	0	0.00	3.44100
Std 1	5	0.83	20.69233
Std 2	10	1.67	36.40763
Std 3	20	3.33	63.77519
Std 4	40	6.67	125.53204
Std 5	60	10.00	208.01977
Std 6	80	13.33	266.16016

Appendix 7. Determination of Tween 20 residues

Table 29. Gravimetric determination of Tween 20 residues from the Soxhlet extract. Methanol was used as the extraction solvent. Two replicate extractions were made from each sample.

Sample	*m* (sample)	*m* (dried extract)	Tween 20 residues
	g	g	mg/g
6 g/l, DM 21 %	1.0039	0.0236	23.51
	1.0107	0.0264	26.12
12 g/l, DM 21 %	1.0193	0.0372	36.50
	0.9757	0.0336	34.44
6 g/l, DM 5.5 %	1.0331	0.0599	57.98
	1.0246	0.0538	52.51
12 g/l, DM 5.5 %	1.0414	0.1037	99.58
	0.9814	0.1033	105.26

Table 30. Results from the spectrophotometric determination of Tween 20 residues. LCK433 cuvette test were used in the measurements.

Sample	*m* (sample)	Dil. coeff.	*A*	*c* (Tween 20)	Tween 20 residues
	g			mg/l	mg/g
6 g/l, DM 21 %	1.0063	1	0.243	8.65	8.60
12 g/l, DM 21 %	0.9999	1	0.297	19.04	19.04
6 g/l, DM 5.5 %	0.5134	1	0.281	15.96	31.09
12 g/l, DM 5.5 %	0.4951	1	0.488	55.77	112.64

Table 31. Determination of Tween 20 residues by HPLC-DAD.

Sample	*m* (sample) g	Peak area mAU*s	*c* g/l	Tween 20 residues mg/g
6 g/l, DM 21 %	1.0039	30.28468	1.441	17.22
	1.0107	35.99559	1.728	20.52
12 g/l, DM 21 %	1.0193	54.12894	2.640	31.08
	0.9757	40.47497	1.953	24.02
6 g/l, DM 5.5 %	1.0331	102.77043	5.086	59.07
	1.0246	79.61945	3.921	45.93
12 g/l, DM 5.5 %	1.0414	180.47118	8.993	103.62
	0.9814	152.74438	7.599	92.91

Table 32. Results from the spectrophotometric determination of Tween 20 residues. LCK333 cuvette tests were used in the measurements.

Sample	DM %	β g/l	*m* (sample) g	Dil. coeff.	*A*	*c* mg/l	Tween 20 residues mg/g
	21.8	6	0.8110	1	0.939	10.34	12.75
	21.0	9	0.5804	2	0.564	5.72	19.71
	20.2	12	0.6053	2	0.804	8.67	28.66
	5.7	6	0.9084	5	0.798	8.60	47.34
	5.5	9	0.8407	10	0.473	4.60	54.70
	5.3	12	0.2776	5	0.410	3.82	68.85

Appendix 8. Determination of 4-DBSA by direct UV absorption

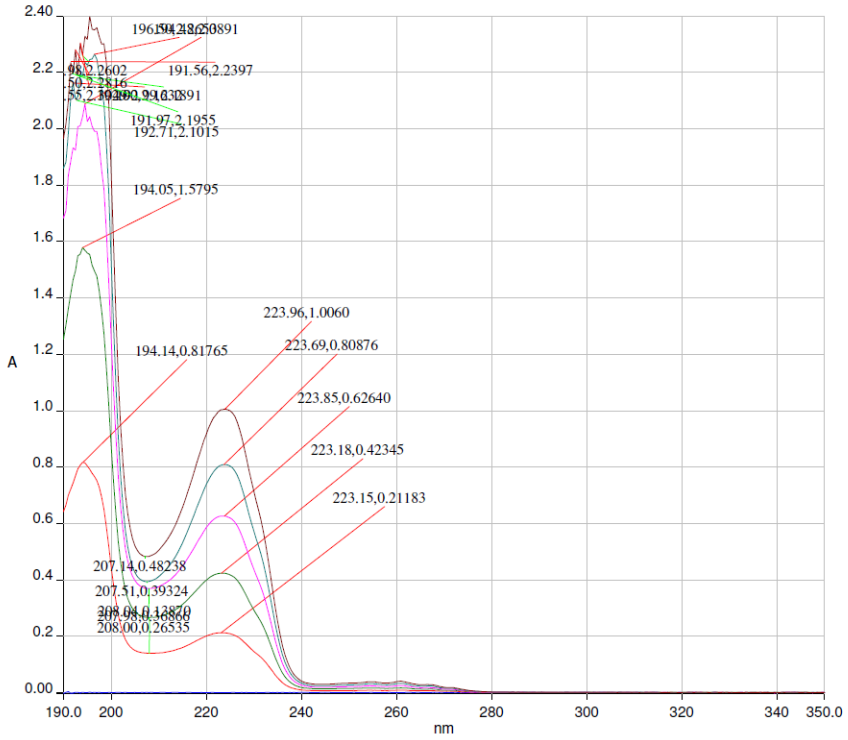

Figure 59. The absorbance spectra of 4-dodecylbenzenesulphonic acid drawn by the program of the spectrophotometer. The graph shows spectra for concentrations of 0, 5, 10, 15, 20 and 25 mg/l and the absorbance maximums for each spectrum.

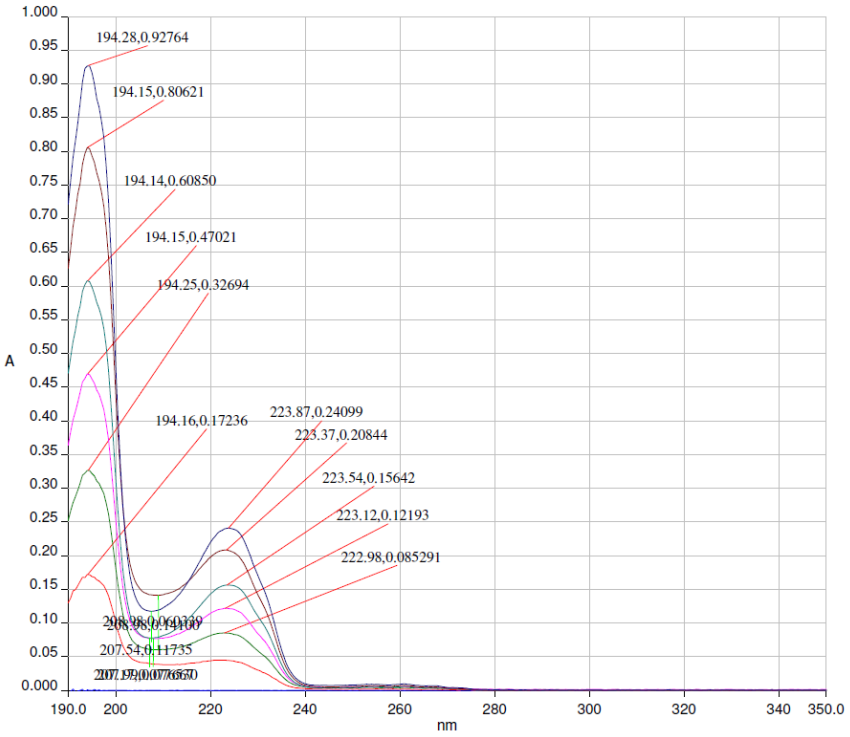

Figure 60. The absorbance spectra of 4-dodecylbenzenesulphonic acid drawn by the program of the spectrophotometer. The graph shows spectra for concentrations of 0, 1, 2, 3, 4, 5 and 6 mg/l and the absorbance maximums for each spectrum.

Table 33. Absorbance measurements of 4-DBSA standards at two different wavelengths: 194 nm and 224 nm. Measurements were conducted by two different spectrophotometers. Table shows the prepared concentrations (mg/l) and absorbance values for both spectrophotometers.

Wavelength	PerkinElmer Lambda 25		Hitachi U-2900	
(nm)	*c* (mg/l)	Absorbance	*c* (mg/l)	Absorbance
194	0.0	0.0000	0.0	0.251
	1.0	0.1727	1.0	0.434
	2.0	0.3228	2.0	0.585
	3.0	0.4683	3.0	0.793
	4.0	0.6129	4.0	0.917
	5.0	0.8011	5.0	1.063
	6.0	0.9316	6.0	1.232
224	0.0	0.0000	0.0	0.098
	5.0	0.2102	5.0	0.296
	10.0	0.4228	10.0	0.505
	15.0	0.6277	15.0	0.708
	20.0	0.8114	20.0	0.919
	25.0	1.0119	25.0	1.122