Kenneth Olesen[1], Caspar van Leeuwen[2] and Fredrik I. Andersson[1]

Revealing Detergent Efficiency and Mechanism by Real-Time Measurement Using a Novel and Tailored QCM-D methodology

Currently there is a lack of knowledge on how to scientifically and rapidly screen new detergent formulations. To address this, we employed the Quartz Crystal Microbalance with Dissipation technique which allows real-time acquisition of the cleaning process. Using an automated multichannel setup enabled rapid, simultaneous screening of eight formulations in regard to cleaning rate, soil swelling and soil removal. Herein, 9 commercially available dishwashing formulations are screened and ranked based on their ability to remove/swell standardized cooking grease soiled onto a silica surface. Moreover, we observed that soil swelling can be monitored *via* the dissipation factor. In summary, we present a real-time *in-situ* method for detergent formulation screening during the R&D phase of new detergents.

Key words: Hard surface cleaning, automatic dishwashing (ADW), detergent, detergency, QCM-D

Aufklärung der Waschmittelleistung und des Mechanismus mittels Echtzeit-Messungen mit einer neuen und maßgeschneiderten QCM-D-Methode. Derzeit besteht keine Erkenntnis darüber, wie man neue Waschmittelformulierungen wissenschaftlich und schnell auswählen kann. Um dieses Problem zu lösen, setzten wir die Quarzkristallmikrowaage mit Dissipationstechnik ein, die eine Echtzeiterfassung des Reinigungsvorgangs erlaubt. Der Gebrauch eines automatisierten Mehrkanalaufbaus ermöglicht ein schnelles simultanes Screening von acht Formulierungen hinsichtlich der Reinigungsgeschwindigkeit, der Schmutzquellung und der Schmutzentfernung. Es wurden auch neun kommerziell erhältliche Geschirrreiniger untersucht und nach ihrer Fähigkeit, Standardküchenfett von Quarzoberflächen zu entfernen bzw. auf ihnen anzuquellen, geordnet. Außerdem beobachteten wir, dass die Schmutzquellung mit dem Verlustfaktor überwacht werden kann. Zusammenfassend stellen wir eine Echtzeit-in-situ-Methode für das Screening von Reinigungsmittelformulierungen während der Forschungs- und Entwicklungsphase von neuen Reinigungsmitteln vor.

Stichwörter: Reinigung harter Oberflächen, maschinelles Geschirrspülen, Reinigungsmittel, Reinigungsleistung, QCM-D

1 Introduction

Cleaning is the process of removing different types of soil from a surface, such for example dishes and glassware. Cleaning is performed by using a cleaning agent that removes the soil or other unwanted substances. Understanding and evaluating detergent formulation cleaning efficiency is of great importance, for example during development of new commercial detergents for hard surface cleaning purposes. The objective of new detergent formulations is to return the soiled surface to the state it had prior to being soiled and this in a fast, environmental friendly and efficient way. Many aspects control how efficient a detergent works for soil cleaning including concentration, temperature, the properties of the water (which carries the detergent to the soiled surface), the detergents affinity for the soil, its ability to penetrate the soil and contact time in-between soil and detergent [1]. The first studies on detergency of detergent formulations date back to pre-1950 by pioneering studies [2]. However, very few standardized ways of evaluating new formulations in regards to their cleaning efficiency exists today, but many methods have been developed for certain well-defined substrate surfaces and soils [3]. Analytical tools often used to judge whether cleaning has been successful or not are simple visual and/or colorimetric techniques [4, 5] before and after soaking in detergent solution. Such technologies are time consuming, require a lot of sample, often imprecise and rely on the human eye [6]. Spectroscopic methods like reflectance and fluorescence have also been used to try to evaluate the detergency of surfactants [7, 8] with the main disadvantage being the background noise emission from the material itself. Even simpler analytical methods such as weighing mass on soiled cleaning plate before and after soaking in detergent solution is common (IKW Methods for ascertaining the cleaning performance of dishwasher detergents). Cleaning efficiency will then be calculated according the following formula: cleaning efficiency (%) = mass soil released from plate/mass deposited on plate. For cleaning of food residues so called Clean-In-Place (CIP) systems such as columns have been developed [9, 10]. Also, pioneering studies using sensing technologies such as SPR to probe detergency do exist but remain in their infancy especially in regards to lack of standardized soils and industry relevant surfaces mimicking cleaning substrates (gold needs to be used with SPR) [6, 11].

Although, the above methods can provide insight into the efficiency of cleaning for new detergent formulations, a proper scientific real-time method to analyze such behavior in an industrial setting is currently lacking. In this paper we propose the Quartz Crystal Microbalance with Dissipation (QCM-D) monitoring to be a novel tool for elucidating cleaning efficiency and swelling ability in real-time, i. e. allowing kinetics from the cleaning process. The strong advantages of the QCM-D technique over existing methods are its extreme sensitivity (detection limit 0.5 ng), multiple different sensor

1 Biolin Scientific AB, Västra Frölunda, Sweden
2 Center For Test materials BV, Vlaardingen, The Netherlands

surfaces (such as for example stainless steel, polystyrene and different glass coatings) and soils to choose from and the ability to probe the effectiveness, swelling and mechanistic action of the detergents in a time-resolved manner. By extracting three QCM-D cleaning parameters (cleaning rate, swelling time and overall mass soil removed) we can easily rank different detergent formulation in an automated way according to cleaning efficiency within a short period of time (ca. 30 min).

2 Experimental Procedure

2.1 QCM-D fundamentals

Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) measures both frequency and dissipation of a sensor comprising a quartz crystal covered with a gold electrode. The sputtered gold area can subsequently be coated with various coatings, for example SiO_2. It is possible to make the quartz crystal oscillate by applying an AC voltage over these electrodes. The crystal's resonance frequency (f) can thus be determined electrically. A change in mass (Δm) on the quartz surface will directly change the resonance frequency (Δf) and can in the simple case be calculated through the Sauerbrey relation: $\Delta m = -C \cdot \Delta f$ (C is the calibration constant of an AT-cut gold crystal). Binding of molecules onto the sensor surface causes the oscillating frequency to decrease (mass uptake), whereas increase in oscillation frequency is interpreted as a mass loss from the surface. When the sensor is coated with floppy adhering layers this relation does not strictly hold but will for thin films give a good approximation.

The dissipation factor (D) is a measure of how much the sensor is damped. It can be measured by shutting off the driving voltage to the crystal and observing how the voltage output from the sensor decays. As a rule of thumb, the higher the dissipation, the more viscoelastic is the adhering film.

2.2 QCM-D measurements and wash cycle definition

All measurements were performed using the Q-Sense Pro instrument (Biolin Scientific AB). The instrument is based on the QCM-D technology which enables a real-time monitoring of mass, thickness and structural changes of molecular layers. Sample data was collected as triplicates and run in a fully automated mode to maximize efficiency and reproducibility. A set of cleaning parameters were extracted from the QCM-D measurement to rank each individual detergent using Q-Sense^{tm} Dfind software. All measurements were performed at a fix concentration of detergents at 4 g L^{-1} and measured at 21 °C.

The cleaning cycle as outline below was programed into the QSoft Pro software.

1. Baseline tap water (10 min)
2. Injection of detergent (40 min)
3. Wash with tap water (20 min)

2.3 Preparation of soiled QCM-D sensors; spin coating of grease soil

Used cooking grease (Center For Testmaterials BV, The Netherlands) was spin-coated onto QSX 303 SiO_2 QCM-D sensors (Biolin Scientific AB) by dissolving 0.25 g in toluene solvent. Spin coater (Laurel Ws-400) was set at 2000 rpm for 20 s. The organic solvents were left to evaporate by incubating the coated sensor at 70 °C for 30 min prior to measurement. Ca. 140 Hz soil was coated onto the sensor and set as 100 % soiled.

2.4 Preparation and grouping of detergents

Detergents were brought to fine powder form by grinding the whole contents of the pre-packed detergent. Subsequently, the detergent was dissolved in Dutch tap water (provided by Center For Testmaterials BV, The Netherlands) at a concentration of 4 g L^{-1}. The tap water had a GH value in-between 8–8.5. A minor amount of non-dissolved material was removed by filtering the detergent solution through a 0.45 µm polypropylene syringe filter (Watman). The 9 commercial detergents were labelled A, B, C, D, E, F, G, H, I and the 10th formulation was labelled reference detergent X. Based on price the 9 different commercial detergents were grouped into three segments:

1. Expensive (detergent A, B, F and G)
2. Mid-priced (detergent D and E)
3. Cheap (detergent C, H and I)

2.5 Analysis of QCM-D data

Frequency changes and changes in dissipation for the 3th overtone were used and data were analyzed using the Q-Sense^{tm} Dfind software using peak-finding algorithms and simple least square method. Swelling time was extracted from raw data using the time of detergent injection typical as reference point and as end point, time at maximum dissipation value for overtone 3 was used. Apparent rate of removal (Hz/s) was given by the steepest slope of the linear regression line when fitted to raw data (washing step).

3 Results and Discussion

3.1 Generation of a homogeneous grease soiled QCM-D sensor

In order to achieve a stable platform for the formulation screening assay, we spin-coated used cooking grease (Center for Testmaterials BV, The Netherlands) onto silica sputtered

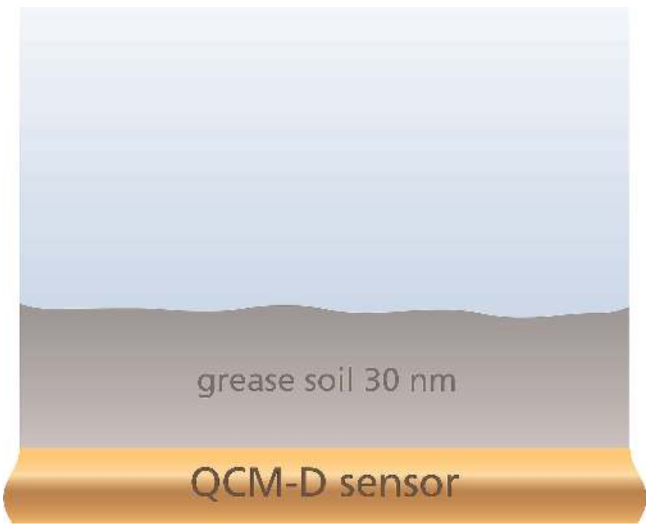


Figure 1 Illustration of soiled silica QCM-D sensor. A 30 nm (530 ng/cm^2) thick grease soil is coated

QCM-D sensors. A homogeneous coating (observed by optical inspection) with a thickness of 30 +/– 3 nm (judged from QCM-D signal) was produced. The soil coating was stable in water as tested by QCM-D measurements in MQ water (data not shown). Moreover, the soiled sensor surface displayed a significant stability over time when stored in inert gas (+8 weeks). Although not shown here, successful coating strategies of several different kinds of soils onto QCM-D sensors (IKW plate test, motor oil, egg yolk, APC burnt in soil and biofilm cultures) have been developed (unpublished data).

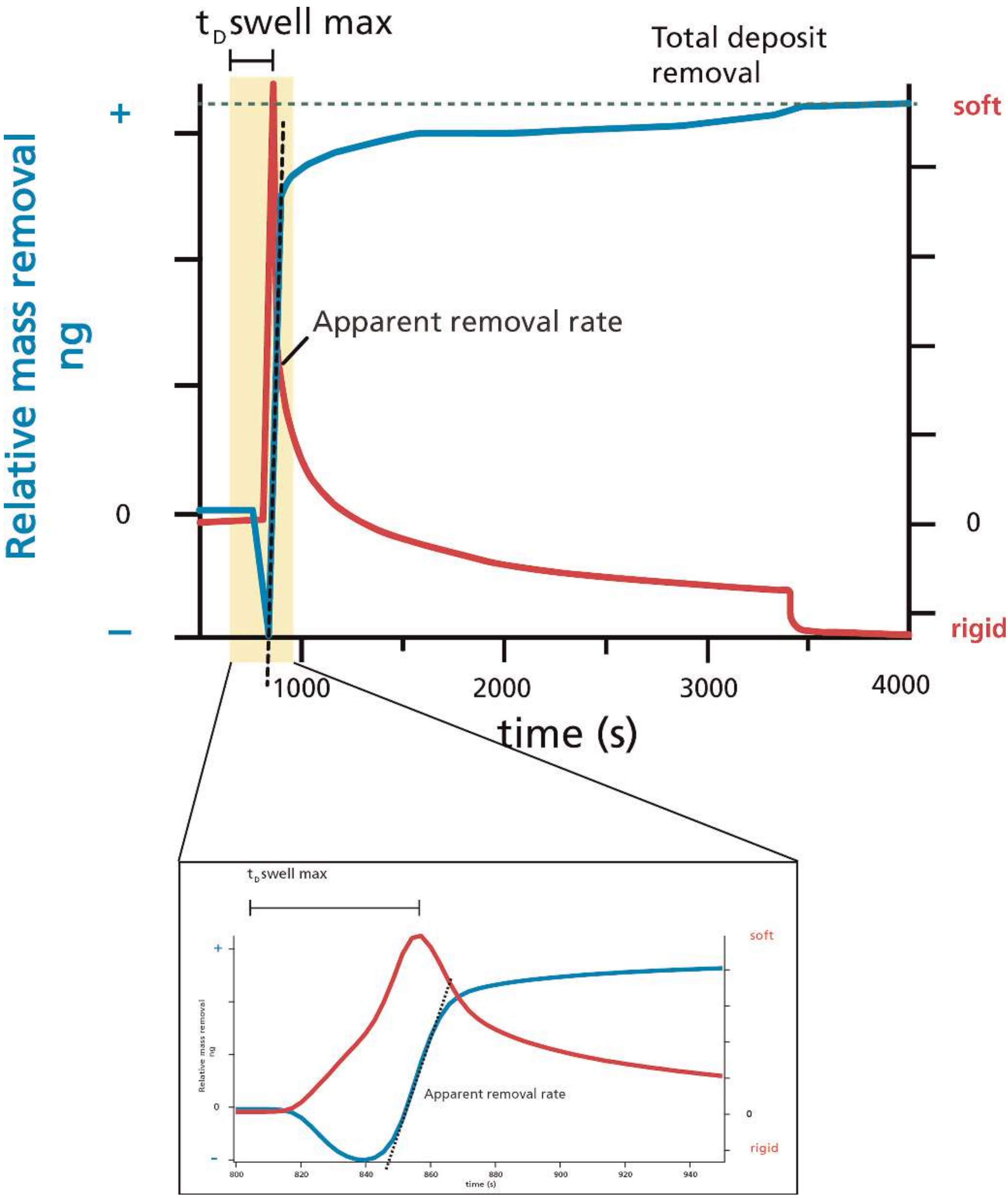


Figure 2 The figure illustrates the typical QCM-D cleaning parameters during a wash cycle (baseline in tap water, injection of detergent and subsequent rinse with water). Frequency depicted in blue and dissipation in red. Injection of detergent approximately at 700 s (inset picture, marked with yellow)

3.2 A typical QCM-D cleaning profile and its parameters

The grease soiled silica sensors were mounted into the QCM-D measuring chamber (Q-Sense^{tm} Pro) and the wash cycle was performed as described in the materials and methods section. The typical QCM-D responses (frequency and dissipation) upon cleaning with a surfactant above critical micelle concentration (CMC) are displayed in Fig. 2.

All tested detergents showed the typical cleaning profile (Fig. 2). The wash cycle could be divided into three distinct steps as judged from the QCM-D data; a pre-rinse step, a detergent adsorption/swelling/cleaning step and a rinse step. During the phase where the detergent molecules bind to the soil stain, the soil undergoes significant swelling/hydration (as indicated in Fig. 2, increase in dissipation and decrease in frequency). This phase is then followed by a fast removal of the soil (Fig. 2, frequency increase (mass loss), dissipation decrease). In most cases all of the coated grease soil is removed, leaving a bare silica sensor after finished wash cycle.

The following parameters were extracted from the QCM-D raw data (Fig. 2.) and used to evaluate and rank the 10 different detergents;

1. *Apparent soil removal rate*: parameter displaying amount of soil removed per time unit (Hz/s)
2. *Total deposit removal*: parameter indicating how much soil that is removed after finished wash cycle (%)
3. t_D *swell max*: parameter indicating how quickly the soil swells after injection of detergent (minutes)

The tested detergents showed differences in all three tested parameters (Table 1), indicating distinct differences in cleaning performance. Interestingly, one can observe that the most expensive ones clearly have the highest apparent removal rate of the grease soil (Table 1). It should be noted that in the current experiment the washing step (injection of detergent) was set to 40 min for all detergents, so even a detergent possessing a very slow apparent removal rate (for example detergent D, Fig. 3, 0.21 Hz/s) will remove close to 100% of soil within that period of time. However, some of the tested detergents showed a very fast apparent removal rate (for example detergent A, Fig. 3, ca. 9 Hz/s) and consequently these detergents could remove the soil in a much shorter time period.

3.3 Monitoring of swelling/hydration of soil; swelling/hydration is a prerequisite for effective cleaning

Another intriguing parameter extracted is the time it took for the soil (now consisting of soil + detergent + associated water molecules) to swell, termed t_D swell max (Fig. 2.). As observed in Table 1, the faster the soil reaches a dissipation maximum (low t_D swell max) the faster is the apparent soil removal rate. That indicates that a good detergent is a detergent that allows effective incorporation of moist/water molecules into the hard fat matrix. This transformation of this solid hard fat matrix to a more soft/hydrated film causes an increase in dissipation. Indeed, this has been indicated by scanning fluid dynamic gauge technique together with gravimetric tests [12]. After swelling the soil can be removed possibly via a so-called roll-up mechanism because the detergent lowers the interfacial tension in-between fat and water. The way QCM-D enables measurement of swelling is *via* the dissipation factor which is unique for the QCM-D technology [13]. By closely analysing the QCM-D cleaning profile of two detergents (detergent D and F) with drastic differences in swelling ability, this hypothesis is strengthened (Fig. 3.). Detergent F has a low t_D swell max (15 min, fast swelling) and a very rapid cleaning rate (ca. 2 Hz/s), whereas detergent D has a high t_D swell max value (ca. 20 min, slow swelling) and display a significant slower cleaning rate (0.2 Hz/s).

3.4 Ratio of f and D: a benchmark value for detergency

The amount of water carried by a particular detergent [14] and the ability through diffusion [12] to incorporate water-detergent complex is directly proportional to the degree of swelling. In QCM-D one can simultaneously monitor the detergent-water uptake by the soil film and swelling of the soil film. In this study we observe that a detergent with a high overall cleaning efficiency/detergency has a ratio in-between mass uptake and dissipation units during the washing step (efficiency ratio = f/D) within the range of 1.2 – 1.5. Moreover, we observed for all studied detergents that the maximum removal rate (Eq. 1.) of soil precisely coincides with the time when maximum swelling has occurred (Eq. 2, Fig. 2, inset picture).

$$\frac{[\partial f]}{[\partial t]} = \max \qquad (1)$$

$$\frac{[\partial D]}{[\partial t]} = 0 \qquad (2)$$

Price	Detergents	Total deposit removal (%)	t_D swell max (minutes)	Rate (HZ/s)
Expensive	A	122.60	13.00	9.73
Expensive	B	99.14	12.51	8.97
Expensive	F	102.69	15.11	1.69
Expensive	G	84.64	13.07	8.40
Mid-priced	D	98.40	19.74	0.21
Mid-priced	E	89.32	13.27	6.15
Cheap	C	113.88	14.21	4.02
Cheap	H	86.50	12.27	0.02
Cheap	I	122.14	17.19	1.39
Cheap	X	68.52	21.65	0.40

Table 1 QCM-D cleaning parameters; total deposit removal, t_D swell max (minutes) and rate (Hz/s)

3.5 Ranking of detergent from QCM-D cleaning parameters

To be able to rank the performance of the tested detergents, all three extracted parameters were analyzed together and summarized in Fig. 4. Each detergent ranked in order of performance for each parameter and was given a value between 1 and 10 (10 is best performing detergent, 1 is the worst). The maximum score was set to 30, indicating that the detergent scoring max value had the best result in all three measured parameters.

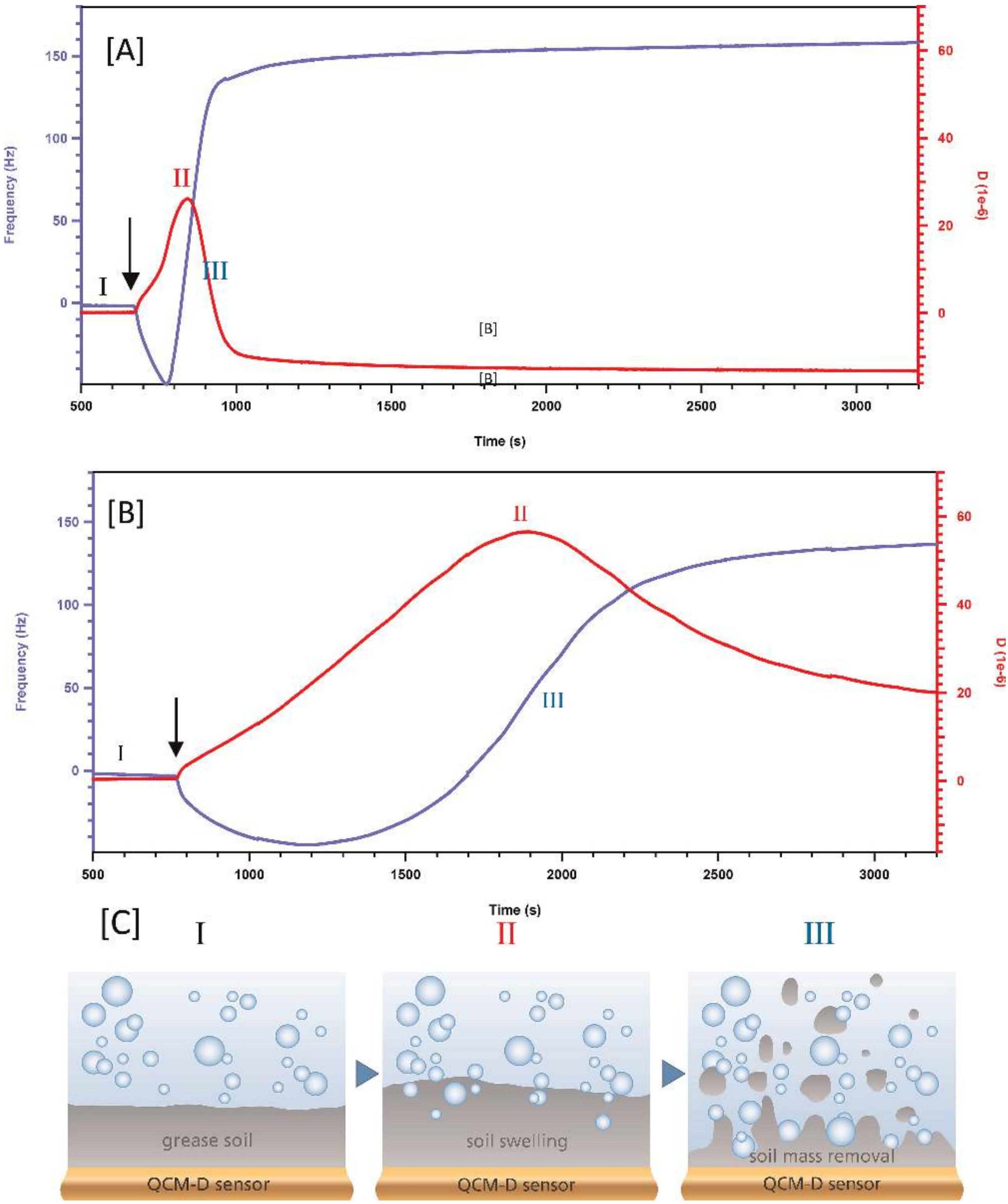
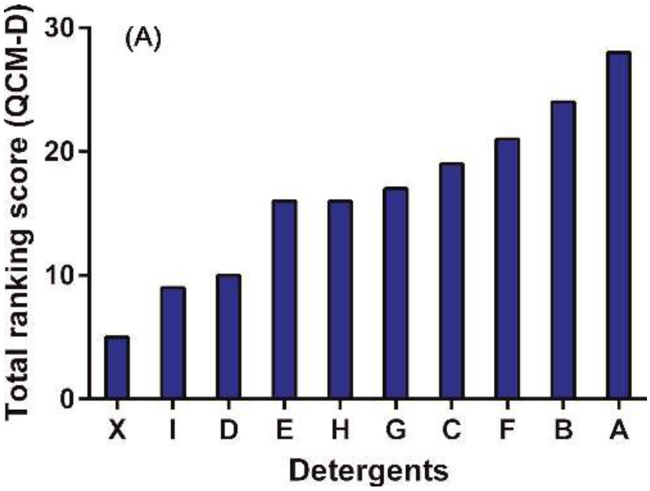


Figure 3 A–C, different cleaning profiles. Panel A: Detergent F, shows a short swelling time coupled to a fast soil removal event, QCM-D raw data is shown as, dark red-dissipation overtone D_3, dark blue-frequency overtone f_3. Panel B: Injection of detergent in panel A–B is marked by downward arrow. Panel C: Schematic illustration of the cleaning process coupled to the observed QCM-D data. The first step is the base-line (detergent free) step, second step shows dynamic uptake of detergent-water complex and subsequent swelling of soil and finally in the third step, removal of soil

Figure 4A strongly suggests that the most expensive detergents (group 1) are actually also the best performing ones. The negative reference detergent X is the worst performing; only reaching a total of 5 out of 30 ranking units. The intermediate priced detergents (group 2) are in-between also in the ranking of cleaning efficiency and the cheap detergents (group 3) are performing almost equally bad as the reference detergent X. In conclusion: There seems to be a strong correlation in-between cleaning performance and price of detergents, with the detergents in group 1 most likely having more advanced and better surfactants/tensides in their formulation mixture than the ones in group 2 and 3. However, it is important to note that this assay is only taking into account the chemical cleaning activity and not the mechanical aspect (such for example silica particles in formulation and mechanical action of a dishwasher) of cleaning. In addition, to correlate the nanoscale QCM-D approach with what is occurring in a dishwasher, we compared head-to-head the QCM-D cleaning parameters with Center For Testmaterials "macro scale" set-up, with an automated continues flow system and subsequent colorimetric analysis. As observed in Fig. 4A and Fig. 4B there is a significant correlation (ca. 60%) between the two techniques which justifies QCM-D as an early R&D screening tool. Interestingly, there are a few outliners (detergent C, D, E and G) which do not cluster well and which could not be explained by standard deviation within the different techniques. However, seeing the extreme differences in-between the two very different analytical techniques in terms of robustness this is not highly surprising.



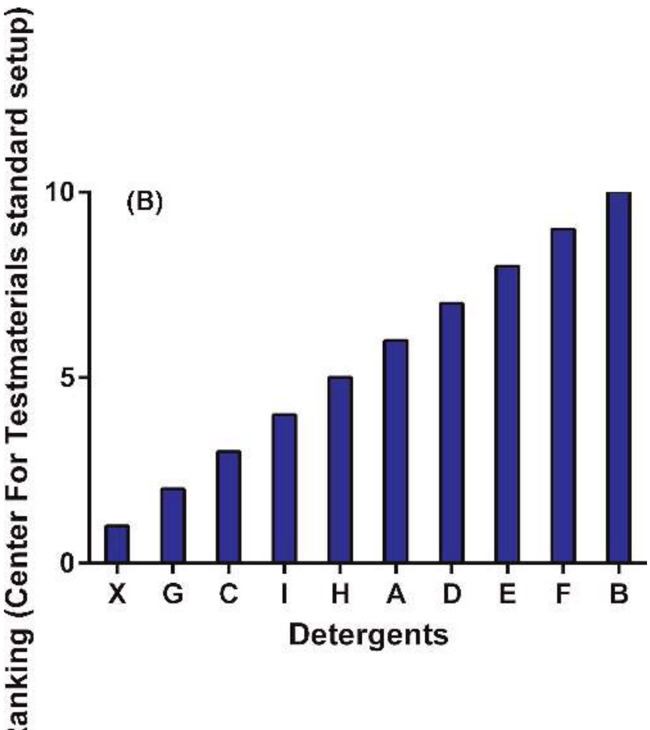


Figure 4 A–B, Ranking of the detergents. Figure 4A; the summation of the three QCM-D cleaning parameter gives a maximum total score of 30. Figure 4B; the ranking achieved by standard method by Center For Testmaterials with an integrated colorimetric analysis

4 Conclusions

In summary, QCM-D is presented as a new methodology for analyzing detergent formulation efficiency in a time-resolved manner. By rapid data analysis of the raw data upon injection of a detergent solution over a grease soil QCM-D sensor, three QCM-D cleaning parameters can be extracted: cleaning rate, swelling time and overall mass removal. By combining the three cleaning parameters a ranking of the screened detergents is easily achieved. Such information is very valuable during the R&D phase of new detergent formulations. By use of the QCM-D technique one can evaluate the cleaning ability of individual constituents of the detergent formulation and consequently new detergent formulation can be specific tailored. We therefore foresee that QCM-D instrumentation should be a valued technology in detergent industry laboratories and aid in faster development of better detergents.

References

1. *Wilson, D. I.*: Challenges in cleaning: recent developments and future prospects. Heat Transf. Eng. *26* (2006) 51–59. DOI:10.1080/01457630590890175
2. *Bacon, O. C.* and *Smith, J. E.*: Detergent action-mechanical work as a measure of efficiency of surface-active agents in removing soil. Ind. Eng.Chem. Res. *40* (1948) 2361–2370. DOI:10.1021/ie50468a028
3. *Chateau, M.-E., Galet, L., Soudais, Y.* and *Fages, J.*: A new test for cleaning efficiency assessment of cleaners for hard surfaces. Journal of Surfactants and Detergents. *7(4)* (2015) 355–362. DOI:10.1007/s11743-004-0318-6
4. *Cutler, G.* and *Kissa, E.*: Detergency: Theory and Technology (Surfactant Science Series, Vol. 20) (1986).
5. *Ilec, E., Simončič, B.* and *Hladnik, A.*: Evaluation of Surfactant Detergency using Statistical Analysis. Textile Research Journal. *79(4)* (2009) 318–325. DOI:10.1177/0040517508090886
6. *Patitsa, M., Pfeiffer, H.* and *Wevers, M. A.*: Surface Plasmon Resonance Optical Fibre Sensor for Testing Detergent Cleaning Efficiency. Journal of Surfactants and Detergents. *18(4)* (2015) 697–706. DOI:10.1007/s11743-015-1698-2
7. *Gotoh, K.*: Evaluation of Detergency Using Artificially Soiled Multifiber Fabrics. Journal of Oleo Science *59(9)* (2010) 477–482. DOI:10.5650/jos.59.477
8. *Bradacs, L. K.* and *Schetelig, W.*: Effectiveness of detergent solutions. Journal of the American Oil Chemists' Society. *41(3)* (1964) 161–167. DOI:10.1007/BF03024636
9. *Fan, M., Phinney, D. M.* and *Heldman, D. R.* Effectiveness of Rinse Water during In-Place Cleaning of Stainless Steel Pipe Lines. Journal of Food Science. *80(7)* (2015) E1490–E1497. DOI:10.1111/1750-3841.12914
10. *Jurado Alameda, E., Bravo Rodriguez, V., Bailón Moreno, R., Núñez Olea, J.* and *Vaz, D. A.*: Fatty Soils Removal from Hard Surfaces in a Clean-in-Place System. Journal of Food Process Engineering. *34(4)* (2011) 1053–1070. DOI:10.1111/j.1745-4530.2009.00527.x
11. *Patitsa, M., Pfeiffer, H.* and *Wevers, M.*: Fast and accurate determination of the detergent efficiency by optical fiber sensors. SPIE 8028, Fiber Optic Sensors and Applications VIII. Vol. 8028 (2011) 13.
12. *Pérez-Mohedano, R., Letzelter, N.* and *Bakalis, S.* Swelling and hydration studies on egg yolk samples via scanning fluid dynamic gauge and gravimetric tests. Journal of Food Engineering. *169* (2016) 101–113. DOI:10.1016/j.jfoodeng.2015.08.014
13. *Rodahl, M., Hook, F., Fredriksson, C., A. Keller, C., Krozer, A., Brzezinski, P.* and *Kasemo, B.*: Simultaneous frequency and dissipation factor QCM measurements of biomolecular adsorption and cell adhesion. Faraday Discussions. *107(0)* (1997) 229–246. DOI:10.1039/A703137H

14. *Schott, H.*: Interactions in the system: Clay-detergent-cellulose. Journal of the American Oil Chemists' Society. *45(6)* (1968) 414–422. DOI:10.1007/BF02655498

Received: 24. 03. 2016
Revised: 21. 06. 2016

Bibliography

DOI 10.3139/113.110445
Tenside Surf. Det.
53 (2016) 5; page 488–494

ISSN 0932-3414

Correspondence address

Fredrik I. Andersson, PhD
Senior Application Scientist
Hängpilsgatan 7, 426 77 Västra Frölunda
Tel.: +46-3 17 69 76 90
Fax: +46-31 69 80 40
E-Mail: Fredrik.Andersson@biolinscientific.com and
fredrik07andersson@gmail.com

Kenneth Olesen
Senior Staff Scientist
Tel.: +46-3 17 69 76 90
Fax: +46-31 69 80 40
E-Mail: kenneth.olesen@biolinscientific.com

The authors of this paper

Fredrik I. Andersson: PhD in protein biophysics. Now Senior Application Scientist at Biolin Scientific AB working with the Q-Sense detergent initiative.

Kenneth Olesen: PhD in chemistry. Now Senior Staff Scientist at Biolin Scientific AB working with the Q-Sense detergent initiative.

Caspar van Leeuwen: CEO for Center For Testmaterials BV in the Netherlands.