



Challenge

Evaluation of the rinsing effectiveness of household and commercial washing machines and washer-dryer combos as described in technical specification PD CLC/TS 50677:2019

Solution

Quick and precise determination of the amount of residual surfactant through UV/Vis measurements with SPECORD 210 PLUS

Determination of Concentration by Means of a Calibration Curve – Exemplified by Surfactant Measurements According to PD CLC/TS 50677:2019

Introduction

A new technical specification for determination of the rinsing effectiveness of clothes washing machines and washer-dryer combos for household use was released in 2020 by the European Committee for Electrotechnical Standardization (PD CLC/TS 50677:2019). It applies to all washing machine manufacturers which are producing for the European market. Herein, the amount of residual linear alkylbenzene sulfonate surfactant (LAS), which was extracted from unstained test swatches after the washing performance test, is determined. LAS is used as a reference material for the total amount of base powder detergent IEC-A*, assuming a fixed linear relation between the quantity of surfactant in total and LAS. This simplification is made due to the easy detection of LAS in UV/Vis measurements at 223 nm and 330 nm with 1 nm spectral bandwidth. The characteristic absorbance of LAS at 223 nm is based on a π - π^* transition of the aromatic group of LAS and enables the determination of the concentration of the detergent.

Initially, a calibration curve is created and the absorbance values are plotted against the concentration of known standards. This calibration curve is then used to determine the concentration of the unknown samples, based on their absorbance values. The challenge is the very low concentration of LAS which is remaining in the samples after the washing procedure – therefore, a very low limit

of detection is required for the measurement. The SPECORD 210 PLUS instruments have a very low deviation of the baseline and high reproducibility, which is vital for the accurate creation of a calibration curve with low concentration values.

Materials and methods

All measurements were performed using a SPECORD 210 PLUS spectrophotometer equipped with a standard cell holder and 10 mm quartz cuvettes. Using the latest ASpect UV software version (1.4.4, other versions of ASpect UV give the same results), absorbance spectra were recorded in the range of 200–350 nm (preliminary studies). For measurements according to the PD CLC/TS 50677:2019 standard, the absorbance of the dissolved reference detergent IEC-A* (base powder, as described in EN 60456:2016) under different concentration was measured (further details see below). The calibration curve was created using the photometry module.

Preliminary studies

In order to exclude any potential effect derived by the cuvettes, preliminary tests were performed. Herein, 10 quartz cuvettes (QS) with the same specifications were compared by measuring the absorbance spectrum of each.

All cuvettes were cleaned using HELLMANEX, rinsed with distilled water and ethanol and gently dried under a continuous air flow. Spectra of cuvettes filled with degassed distilled water were measured against air (empty chamber). Upon detailed evaluation, only the cuvettes with the smallest deviation (ΔA) from each other were selected for further measurements.

Standard preparation

The reference detergent IEC-A* was taken as described in Annex A of the technical specification. The distilled water, which was used for the stock and standard preparation, was filled into a volumetric flask at room temperature for at least 24 hours to ensure that it was degassed. All further experiments were performed using the degassed distilled water.

Preparation of Stock 1 (St1):

Approximately 10 g of IEC-A* were weighed (mass was recorded up to 3 decimals), transferred to a 1 L volumetric flask and filled up to 1 L with distilled water. The flask was stirred for about 45 minutes.

Preparation of Stock 2 (St2):

Approximately 10 mL of stock solution 1 were taken while stirring and transferred to a 100 mL volumetric flask. The mass was recorded up to 3 decimals. Then the flask was filled up to 100 mL with distilled water. The flask was stirred for about 15 minutes.

Preparation of Working Standards (WS):

For all working standards stock solution 2 was transferred into a 100 mL volumetric flask while stirring, the mass was recorded to 3 decimals and filled up with distilled water. The volume of stock 2 which was used is shown in Table 1.

Table 1: Working standard data

| Working standard | Target volume of stock 2 in mL (approx.) | Target concentration in mg/L (approx.) | Mass of stock 2 added in g | Concentration calculated in mg/L* |
|------------------|--|--|----------------------------|-----------------------------------|
| WS000 | 0 | 0 | 0 | 0 |
| WS010 | 1 | 7.7 | 0.980 | 7.616 |
| WS020 | 2 | 15.4 | 1.980 | 15.387 |
| WS050 | 5 | 38.5 | 4.943 | 38.412 |
| WS100 | 10 | 77.0 | 9.910 | 77.011 |
| WS250 | 25 | 192.5 | 24.838 | 193.016 |

* calculated as described in PD CLC/TS 50677:2019

The standards were measured with the settings below. As reference air was used, the blank was measured with distilled water.

Instrumentation

To meet the conditions required by PD CLC/TS 50677:2019 the measurements were performed by using a SPECORD 210 PLUS spectrophotometer, because it is a double beam instrument with the possibility to set a spectral bandwidth of 1 nm.

Accessories:

- 10 mm quartz cuvettes
- Standard cell holder

Instrument and software settings

The instrument warmed up for about one hour before the measurement started. Following method settings of photometry module in the SPECORD PLUS software Aspect UV 1.4.4 were used for the measurements:

- Measurement mode: Absorbance
- Wavelength [nm]: 223 and 330
- Integration time [s]: 0.1
- Spectral bandwidth [nm]: 1.0
- Multiple measurement: 3
- Regression: $y = A+B*x$

Measurement

The standard shall be measured within 24 hours after the preparation. The reference was measured against air. For the blank and standard measurement two matching quartz cuvettes were used. To start with, the cuvettes were filled with distilled water for the blank measurement, one was placed in the measurement beam of the instrument, the other one in the reference beam.

The cuvette in the reference beam stayed in the sample compartment. The other cuvette was taken out and rinsed three times with the selected working standard. After rinsing, the cuvette was filled with the working standard and the absorbance was recorded. The rinsing and filling steps were repeated for each working standard.

Results and discussion

Preliminary studies

In order to achieve an R^2 -value of at least 0.9995, as required by the technical specification (PD CLC/TS 50677:2019), several preliminary tests were performed. Initially, the cuvettes and the degassed distilled water were checked for impurities. Therefore, all cuvettes were initially cleaned and subsequently filled with distilled water. It is important to check the purity of the cuvettes, which is a time-saving procedure prior to every measurement. Additionally, it is important to check the cuvettes with the solvent which is also used for the measurements, as some impurities or deviations of the cuvettes are weakened or intensified depending on the polarity of the solvent. Therefore, reference spectra of all cuvettes were recorded, checking for deviations and significant absorbance exceeding 0.002 A between 220 nm and 350 nm.

For all following tests, the cuvettes with the smallest deviation (ΔA) from each other were used and it was made sure that the orientation of the individual cuvettes remained the same. Under the above determined conditions, a spectrum of the reference detergent IEC-A* was recorded in the highest concentration of the working standard (WS250) with a spectral bandwidth of 1.0 nm, as shown in Figure 1. Additionally, WS250 was also measured with different spectral bandwidths, and the difference of the absorbance values at a bandwidth of 1.0 nm and 2.0 nm are within the tolerance of the cuvettes. Consequently, the use of SPECORD 200 PLUS with a spectral bandwidth of 1.4 nm also provides reliable results.

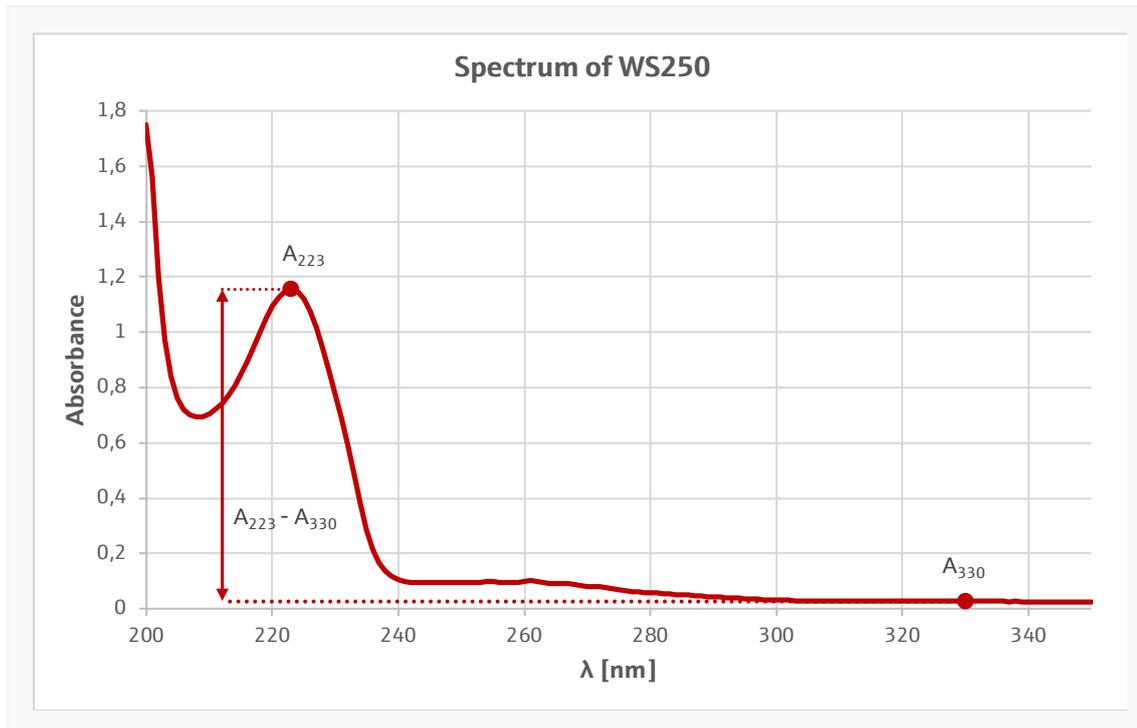


Figure 1: UV/Vis spectrum of WS250 with 1.0 nm spectral bandwidth and degassed distilled water as reference

Generating the calibration curve

After the above described preliminary studies to minimize sources of error, the working standards were measured. As described in the technical specification, the calibration curve was created with the net absorbance which is calculated by $A_{223} - A_{330}$. The software ASpect UV can automatically create calibration curves according to customized formulas (Figure 2). The calibration curve was generated in the photometry module with the calibration settings below.

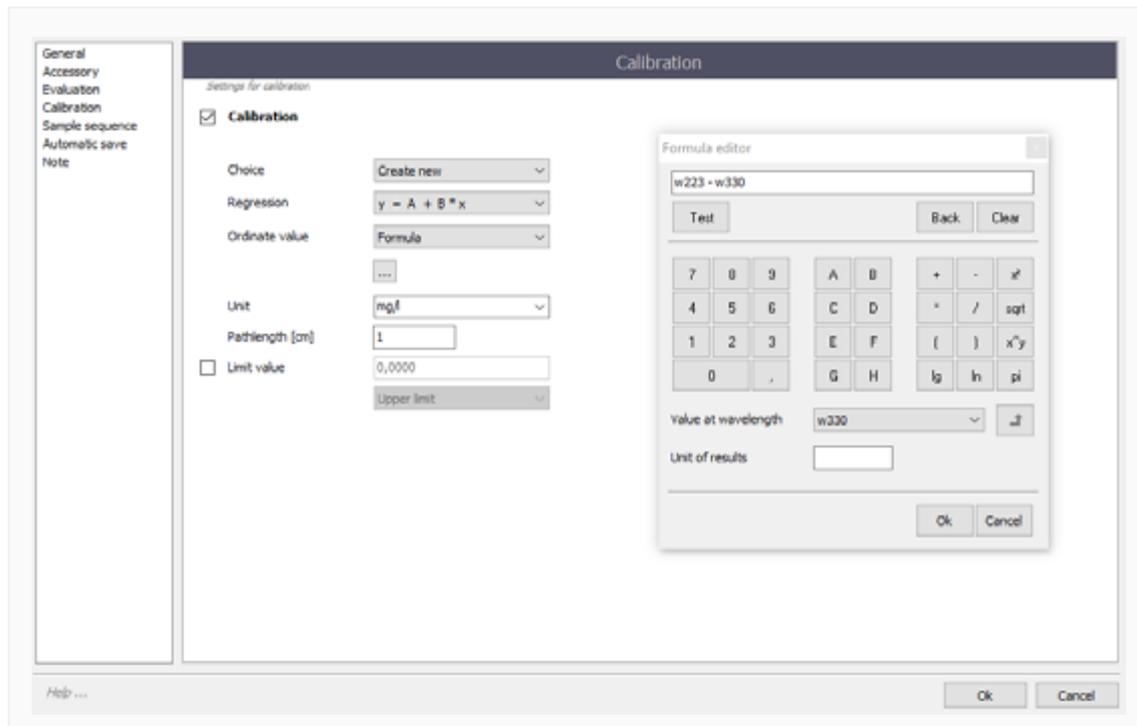


Figure 2: Calibration curve settings in ASpect UV 1.4.4

All working standards had been measured three times at 223 nm and 330 nm. The results can be seen in Table 2.

Table 2: Repetitive measurement of the working standards at 223 nm and 330 nm for the calibration curve

| Working standard | 223 nm 1 st value | 223 nm 2 nd value | 223 nm 3 rd value | 330 nm 1 st value | 330 nm 2 nd value | 330 nm 3 rd value |
|------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| WS000 | 0.0001 | -0.0003 | 0.0001 | -0.0001 | -0.0001 | 0.0002 |
| WS010 | 0.0495 | 0.0491 | 0.0494 | 0.0032 | 0.0029 | 0.0033 |
| WS020 | 0.1005 | 0.1003 | 0.1009 | 0.0065 | 0.0063 | 0.0070 |
| WS050 | 0.2460 | 0.2463 | 0.2475 | 0.0149 | 0.0151 | 0.0152 |
| WS100 | 0.5043 | 0.5036 | 0.5041 | 0.0341 | 0.0339 | 0.0340 |
| WS250 | 1.2402 | 1.2414 | 1.2441 | 0.0807 | 0.0804 | 0.0809 |

The values of the net absorbance ($A_{223} - A_{330}$) are shown in Table 3. Additionally, the average values and standard deviations were calculated.

Table 3: Net absorbance of the working standards for the calibration curve

| Working standard | 1 st value | 2 nd value | 3 rd value | Average | Standard deviation |
|------------------|-----------------------|-----------------------|-----------------------|---------|--------------------|
| WS000 | 0.0002 | -0.0002 | -0.0001 | 0.0000 | ± 0.0002 |
| WS010 | 0.0463 | 0.0462 | 0.0461 | 0.0462 | ± 0.0001 |
| WS020 | 0.0940 | 0.0940 | 0.0939 | 0.0940 | ± 0.0001 |
| WS050 | 0.2311 | 0.2312 | 0.2323 | 0.2315 | ± 0.0007 |
| WS100 | 0.4702 | 0.4697 | 0.4701 | 0.4700 | ± 0.0003 |
| WS250 | 1.1595 | 1.1610 | 1.1632 | 1.1612 | ± 0.0019 |

Additionally, the tolerance of the cuvettes had been calculated and compared to the standard deviations of the triple measurements. The results are depicted in Table 4. It is apparent that the standard deviation is in the range of the tolerance of the 10 mm cuvettes. The low deviation of the individual measurements is due to the low baseline noise of the SPECORD 210 PLUS. This helps to avoid time consuming multiple measurements, as the individual measurements are highly precise.

Table 4: Comparison of the standard deviation of the measurements and the tolerance of the cuvettes for WS250

| | 223 nm | 330 nm | Net absorbance |
|--------------------------------|----------|----------|----------------|
| Absorbance | 1.2419 | 0.0807 | 1.1612 |
| Standard deviation measurement | ± 0.0016 | ± 0.0002 | ± 0.0019 |
| Tolerance of the cuvettes | ± 0.0012 | ± 0.0001 | ± 0.0012 |

The software ASpect UV 1.4.4 automatically creates the calibration curve of the net absorbance by adding the formula ($A_{223} - A_{330}$), as shown in Figure 2. The resulting calibration curve of the net absorbance against concentration is shown in Figure 3 and Figure 4 and an excellent R^2 -value of 1 was achieved. Due to the high precision of the instrument, the R^2 -values of each individual measurement were also very good with R^2 -values of 0.9999.

As no real washing samples were available, the washing samples (e.g., swatches) were simulated with three diluted solutions of IEC-A*. Absorbance spectra of all three samples were recorded three times and the LAS concentration was calculated with the help of the calibration curve (Figure 3, Figure 4 and Table 5). As the calibration curve was created using the formula $A_{223} - A_{330}$, the samples are automatically also evaluated using this formula, which helps to avoid time consuming calculations or even calculation errors.

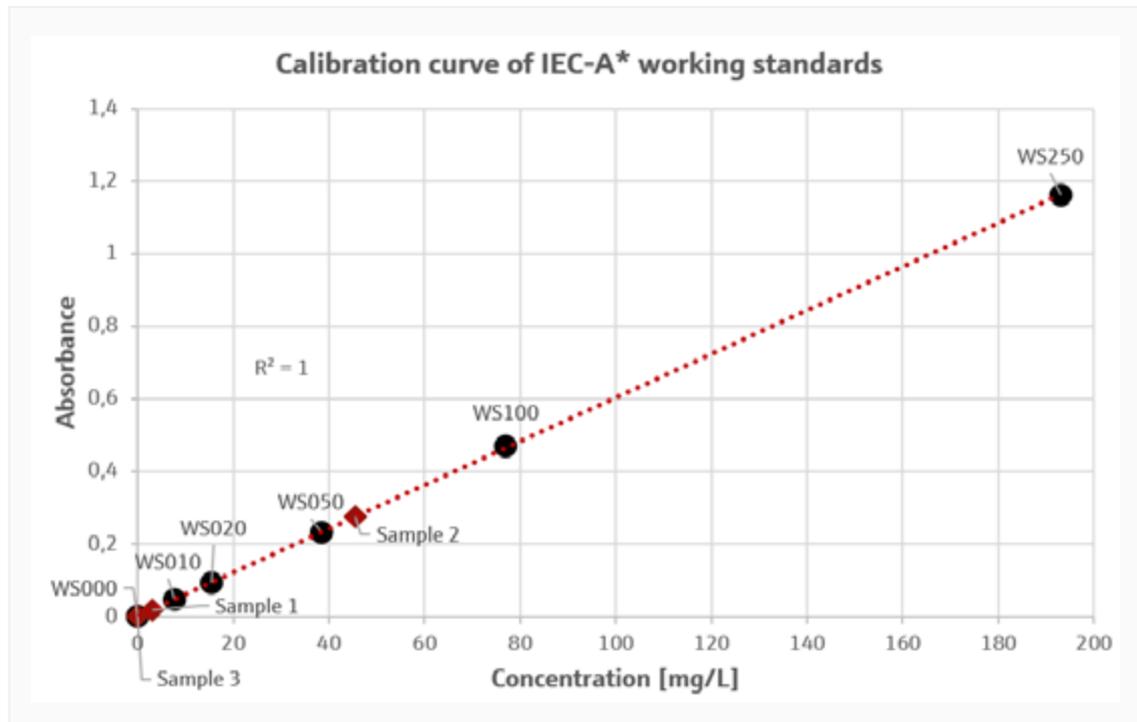


Figure 3: Calibration curve of the IEC-A* working standards WS000 to WS250 (black dots); linear regression with an R^2 -value of 1 (red dotted line) and corresponding samples 1-3 (red rhombus)

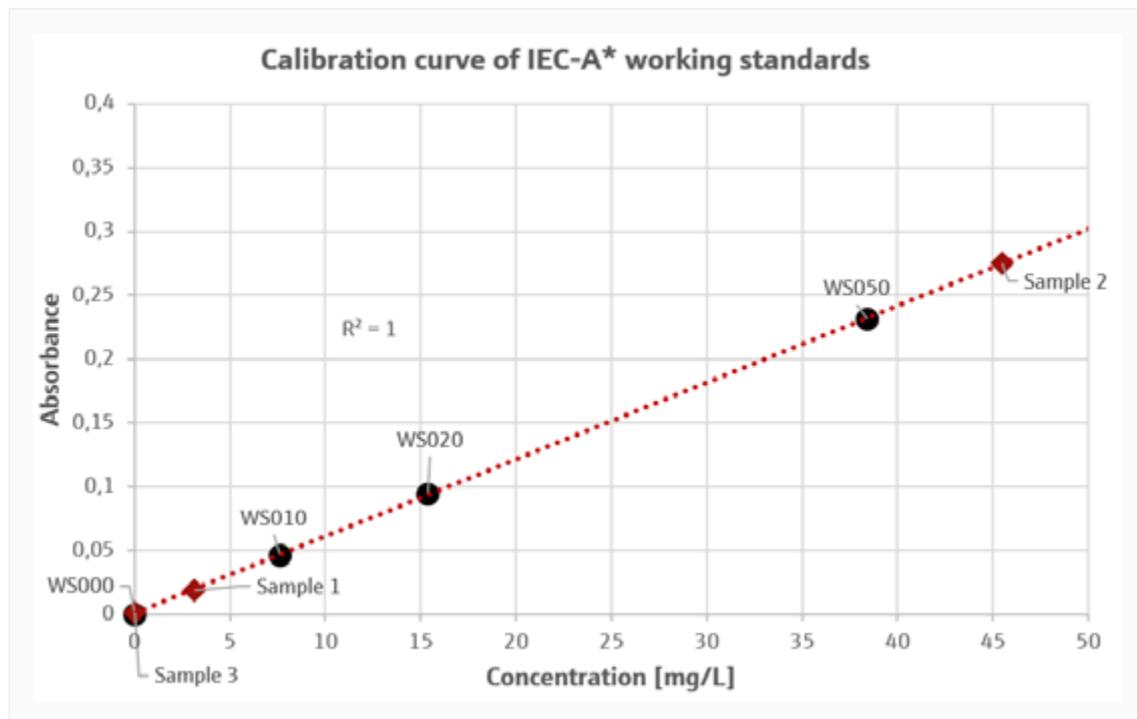


Figure 4: Enlarged view of Figure 3 in the low concentration range (0-50 mg/L)

Table 5: Calculated concentration of the diluted IEC-A* samples (in average) based on the absorbance measurements

| | | Sample 1 | Sample 2 | Sample 3 |
|----------------------|-----------------------------|----------|----------|----------|
| Absorbance | 1 st measurement | 0.0215 | 0.2945 | 0.0017 |
| | 2 nd measurement | 0.0211 | 0.2931 | 0.0014 |
| | 3 rd measurement | 0.0218 | 0.2956 | 0.0019 |
| | Average | 0.0214 | 0.2944 | 0.0016 |
| | Standard deviation | 0.0003 | 0.0010 | 0.0002 |
| Concentration [mg/L] | | 3.11 | 45.51 | 0.04 |

Conclusion

The sample preparation and UV/Vis measurements according to technical specification PD CLC/TS 50677:2019 were performed using the spectrophotometer SPECORD 210 PLUS and the procedure was evaluated. Several preliminary studies have been performed in order to figure out the best and easiest way to obtain reliable calibration curves with low limits of detection and a high R^2 -value.

A time-saving method for preliminary tests to check for the cuvette and solvent purity was presented in this application note. Additionally, time-consuming multiple measurements can be avoided when using the SPECORD 210 PLUS instrument. The high accuracy and precision of the spectrophotometer results in good and reliable values even with a single measurement. Furthermore, the software ASpect UV 1.4.4 supports the automatic creation of the calibration curve with a formula, thus reducing time consuming calculations which are also prone to errors. In addition, the application of the SPECORD 200 PLUS instrument is also possible, as comparison spectra with different spectral bandwidth had been performed and the difference in absorbance for the wavelength in question for different spectral bandwidth is negligible. For large sample throughput, the usage of additional accessory such as cell changers, cell carousel or the autosampler APG is recommended.

The calibration curve of IEC-A* in according to technical specification PD CLC/TS 50677:2019 was created and some test samples had been analyzed. Due to the extensive preliminary studies and the high precision of SPECORD 210 PLUS, a very good R^2 -value of 1, and therefore very reliable values, even after time-saving single measurements, could be achieved.

References

BSI Standards Publication; Clothes washing machines and washer-dryers for household and similar use – Method for the determination of rinsing effectiveness by measurement of the surfactant content at textile materials. PD CLC/TS 50677:2019.

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