



Practice Report

>PHOTOMETRY >CUVETTE TEST
Laboratory Centre, Most



Determination of anionic surfactants using cuvette test LCK332

Problem

A method according to CSN EN 903 (identical to EN 27888:1993) was previously used to determine anionic surfactants. The method is quite laborious; repeated extraction with toxic chloroform has to be carried out.

Solution

The Laboratory Centre in Most took advantage of the offer made by HACH LANGE and tested the cuvette test LCK332. This test is aimed at simplifying and accelerating the determination of anionic surfactants, additionally reducing contamination of the environment with chloroform.

Benefits

The advantages of the cuvette test analysis are the simplicity and speed of determination and the prevention of potential contamination of the environment with chloroform.

Initial situation

Determination according to Czech technical standard CSN EN 903

Previously, the method used to determine anionic surfactants was in accordance with standard "CSN EN 903 Water quality – Determination of anionic surfactants by measurement of the methylene blue index (MBAS)" modified with ISO 7875-1:1984. The principle of the determination is that anionic surfactants react with methylene blue in an alkaline medium. This reaction results in salts that are extracted using chloroform. The method was used primarily for determination of anionic surfactants in raw waters according to legislative requirements.

The method is quite laborious; repeated extraction with toxic chloroform has to be carried out. Besides it is necessary and challenging to thoroughly clean the laboratory glass being used. Despite all the precautions taken, i.e. using an extraction hood, it was not possible to prevent contamination of the environment because the measurement is carried out in cuvettes with an optic length of 50 mm, and the sample needs to be decanted into them.

Workplace / Laboratory

Determination of anionic surfactants in raw and waste waters using the HACH LANGE LCK332 cuvette test is carried out at the quality control division of a waterboard association. The method is accredited by Czech Accreditation Institute.

- Determination of anionic surfactants is performed on site for 100 wastewater samples and 100 surface water samples every year.
- Requirements for determination of anionic surfactants in raw and wastewater are based on legislation as well as customer requirements.
- Determination in industrial wastewater is carried out based on the water authority's requirements. The water authority sets the maximum permissible level of water pollution. Determination in surface water is based on the requirements in valid legislation.

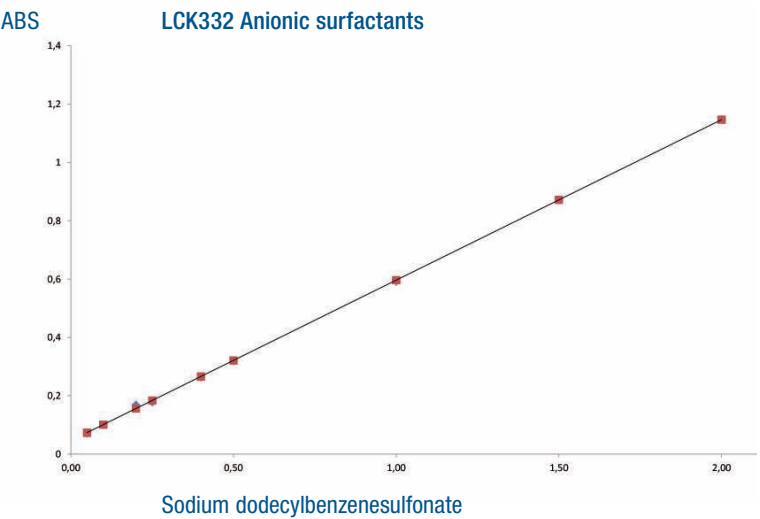
Determination of anionic surfactants using LCK332

The Laboratory Centre took advantage of the offer made by HACH LANGE and tested the cuvette test LCK332, aimed at simplifying and accelerating determination of anionic surfactants and reducing contamination of the environment with chloroform. The above-mentioned test enables determination of anionic surfactants within a measuring range of 0.05 to 2.0 mg/L.

Measurement is easy: 3.5 mL of the sample is dosed into a cuvette with a 13-mm diameter, and then two reagents, which are part of the LCK332 cuvette test, are added gradually. The sample is given a thorough shake

and, after a short wait for the individual phases to separate in accordance with the attached procedure, it can be measured using a spectrophotometer. Absorbance of the separated organic phase is measured at a wavelength of 653 nm. Subsequent evaluation is carried out according to the calibration curve.

The Laboratory Centre carries out the measurements using its own calibration curve (Graph 1) programmed into the HACH LANGE Spectrophotometer DR 5000.



Graph 1:
Calibration Curve
Linear regression relationship:
 $y(\text{abs}) = 0.046231 + 0.549236 \cdot x (\text{conc.})$
 $r = 0.99995$

Validation of the method for determination of anionic surfactants using cuvette test LCK332

Method	LCK332	CSN EN 903
Validation characteristics	Value	Value
Wavelength	653 nm	650 nm
Measuring range (for sodium dodecylbenzenesulfonate) [mg/L]	0.05–2.0	0.05–0.4
Sensitivity [L/mg]	0.549	2.599
Limit of detection [mg/L]	0.024	0.020
Limit of quantification [mg/L]	<0.05	<0.05
Bias observed [%]	6.17	2.20
Max. observed repeatability coefficient of variation 0.05 mg/L [%]	8.42	3.05
Intermediate standard deviation for the control standard 0.2 mg/L [%]	4.71	5.80
Uncertainty across the operating range [%]	21	14

Table 1: Validation characteristics

The method for determination of anionic surfactants using the cuvette test was validated for wastewater, surface water and ground water. Validation characteristics are indicated in Table 1. Comparison of the results of the cuvette test LCK332 with the results obtained by analysis using the procedure specified in CSN EN 903 formed a part of the validation.

Analyses of real samples of surface, ground and waste waters

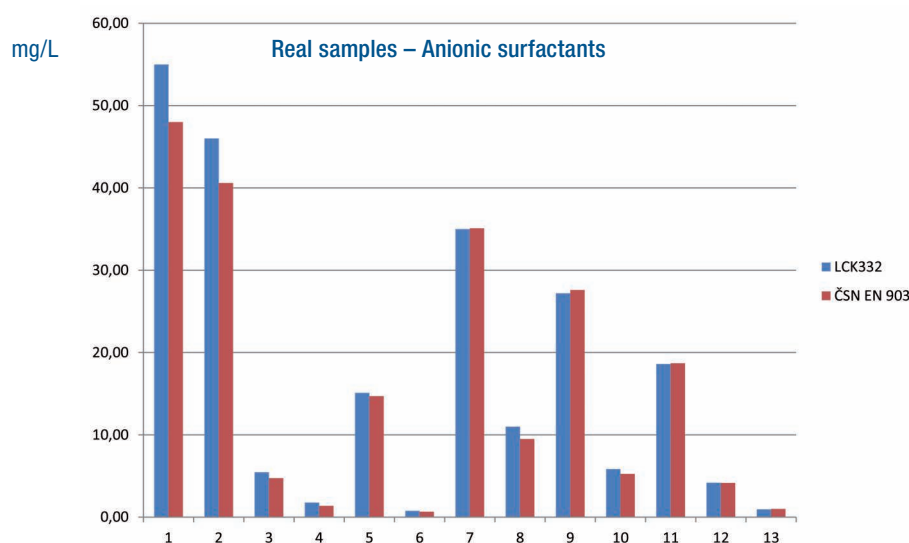
Analyses were carried out on real samples of ground and surface water. In general, no anionic surfactants are detected in these waters, so the detected values of anionic surfactants in all samples determined using both methods were below the limit of determination, i.e. less than 0.05 mg/L.

Analyses on selected waste water samples were carried out using both methods as well, i.e. using the cuvette test LCK332 and according to CSN EN 903. For the overview of the results as well as a graphic representation in bar graph form, see Table 2 below (Graph 2). Method recovery using wastewater samples with standard addition was 99 %.

Results were analysed using the pairwise comparison method and the significance test for differences between pairs, i.e. the significance test for average differences, was also carried out. The test concluded that the differences were insignificant.

Sample no.	1	2	3	4	5	6	7	8	9	10	11	12	13
Concentration LCK332 [mg/L]	55.00	46.00	5.46	1.77	15.10	0.77	35.00	11.00	27.20	5.84	18.60	4.18	0.95
Concentration CSN EN 903 [mg/L]	48.00	40.60	4.74	1.38	14.70	0.67	35.10	9.50	27.60	5.26	18.70	4.16	1.00

Table 2: Results of real sample determinations



Graph 2: Representation of Table 2 in bar graph form

Benefits

Advantages of analysis using the cuvette test are as follows:

- Simplicity and speed of determination
- Prevention of possible contamination of the environment with toxic chloroform
- Increased safety for lab workers
- Minimum amount of toxic waste

Conclusion

The aim of determining the anionic surfactants in surface, ground and wastewater using two methods, i.e. the cuvette test LCK332 and the standard method according to CSN EN 903, was to then compare the results of both methods. Based on the results of the analyses and statistic tests, we can confirm that there were no significant differences between the two methods.

The advantages of the cuvette test analysis are the simplicity and speed of determination and the prevention of potential contamination of the environment with chloroform. Thanks to that a greater safety of lab workers is ensured. The laborious and time consuming determination of anionic surfactant according to CSN EN 903 consists of repeated chloroform extraction and sample handling for approximately one hour, so it is quite challenging to carry out this determination for more than three samples in parallel. Using cuvette tests the extraction is carried out only once and without any difficulties for larger sample series.

Dosage of low sample volume is the only disadvantage of the cuvette test; higher dilution, if possible, may increase the uncertainty of the determination. However, the wider measuring range needs less dilution. Uncertainty of the results according to CSN EN 903 is 14 % within the operating range of 0.05–0.4 mg/L. A 21 % uncertainty was determined for LCK332 and its wider operating range of 0.05–2.0 mg/L.

A single determination of anionic surfactants according to ČSN EN 903 creates more than 300 mL of the toxic waste. The great advantage of the cuvette test is that it creates a minimum amount of toxic waste which remains in the closed cuvettes. Recycling and disposal of used cuvette tests is offered by HACH LANGE.

Additional HACH LANGE products are used by the quality control division, such as cuvette tests for determining the total nitrogen in wastewater; additional spectrophotometers used are DR 2000, DR 2800, DR 4000, DR 5000 and the QUIKCHEM 8500 flow injection analysis system.



UV-VIS Spectrophotometer DR 5000



The LS 120 Shaker automatically extracts the organic phase of up to 8 cuvettes in parallel.