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Rapid Determination of Anionic Surfactants by Improved Spectrophotometric Method Using Methylene Blue

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A rapid and simple method for the determination of anionic surfactants in tap water has been developed. The official analytical method in Japan for the determination of anionic surfactants in tap water requires tedious procedures and requires large amounts of chloroform as the extract solvent; it was greatly improved by the present spectrophotometric method using Methylene Blue. Our present method requires only one half of sample (50 ml), one tenth of the extraction solvent (chloroform=5 ml), and one sixth of the analytical time compared with the official analytical method.

Keywords Rapid determination, anionic surfactants, Methylene Blue, chloroform, spectrophotometry, tap water

Surfactants, especially anionic surfactants (AS hereafter), which are now essential for our dairy life, sometimes cause water pollution of water-supply source, such as rivers and lakes, and attract attention as one of the factors which affect natural ecosystem. Therefore, it is important to determine the concentration of AS accurately. However, the official analytical method in Japan for the determination of AS in tap water requires tedious procedures, and requires large amounts of chloroform as the extract solvent. We have thus tried to improve the official method to obtain AS concentration rapidly and accurately. Although there are various kinds of commercially available surfactants, the most frequently used ones are AS (78% in Japan (1990)[1]). Among many kinds of AS, esters of fats and oils·higher fatty acid or sulfuric acid, alkylsulfates, alkylsulfonates, and naphthalene sulfonate are representatives of the AS. The total of these five surfactants shares around 90% of total amount of products of AS in Japan (1991).[1] Above all, sodium dodecylbenzenesulfonate shares 63% of the anionic surfactants in Japan, and is specified as a standard AS in the official analytical methods for tap water in Japan. Thus, we chose sodium dodecylbenzenesulfonate (DBS hereafter) as the representative of AS and started research.

AS has usually been determined by spectrophotometric methods[2-18], using Methylene Blue (MB spectrophotometry hereafter). This method has been employed in the standard method (Japan)[2] for the determination of AS in tap water or samples of water supplies. However, as already stated, MB spectrophotometry in the current standard method requires lengthy procedures and takes a long time. In addition, a large amount of chloroform is used as the extractant, which has a harmful effect on chemists and the environment. Mae[13], for example, tried to improve the MB spectrophotometries specified in the Japanese Industrial Standards methods.[14,15] However, this method involves the processes of double extraction of an ion pair of AS and MB, and the problem of complicated procedures was not solved. Recently, a few methods[16,17] which aim to reduce the reagent quantities by using sodium dodecylsulfate as a standard anionic surfactant, and another method[18] which uses a certain kind of adsorbent, have been proposed; however, all of these methods still involve tedious procedures.

In the present study, MB spectrophotometry, specified in the official standard methods[2] for the determination of AS in tap water, were examined in detail, and finally we found a rapid and simplified method that requires half volume of the sample water, one tenth of the solvent volume and one sixth of the analytical time compared with the official standard method in Japan.

Experimental

Reagents

Sodium dodecylbenzenesulfonate as a representative of AS used in the present study was commercially obtained from Wako Pure Chemical Industries, Ltd. (DBS[$C_{12}H_{25}C_6H_4SO_3Na$]; purity 99.0% or higher,) and used without further purification. Methylene Blue (trihydrates), used as a cationic dye, was commercially

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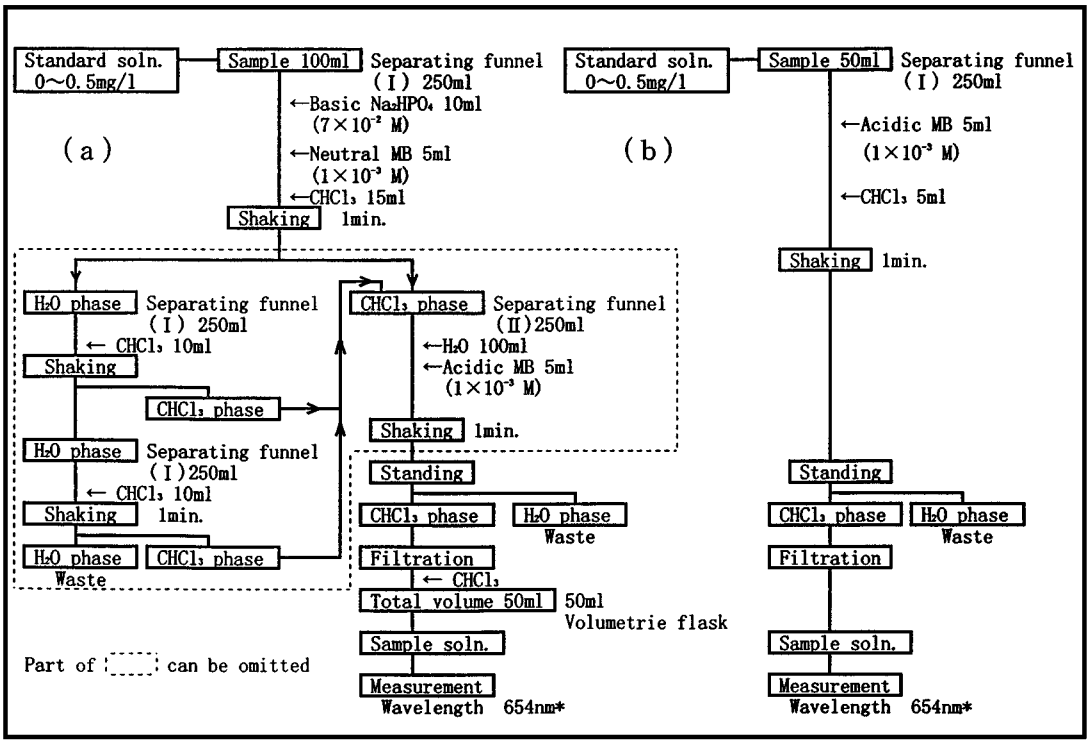

Fig. 1 Experimental procedures of the official method in Japan (a) and the present method (b) for the determination of anionic surfactants in tap water using Methylene Blue. *: Cell length=10 mm.

obtained from Wako Pure Chemical Industries, Ltd. (MB[$C_{16}H_{18}N_3SCl \cdot 3H_2O$]; purity 98.5% or higher) and was used without further purification. For other reagents, analytical grade reagents were commercially obtained.

(1) DBS standard solution. The required quantity of DBS was dissolved in pure water and diluted to a 1.0×10^{-3} M DBS solution (M=mol/l); this was stored as a DBS standard solution. This standard solution was diluted to the desired concentration before use.

(2) Acidic MB standard solution. A required quantity of MB (0.35 g) was dissolved in pure water (500 ml), and 6.5 ml of concentrated sulfuric acid was added; the solution was diluted to the mark of a one-liter volumetric flask with pure water to prepare a 10^{-3} M MB standard solution. This solution was diluted to the desired concentration before use.

(3) Neutral MB standard solution. The required quantity of MB (0.35 g) was dissolved in pure water (500 ml), and the solution was diluted to the mark of a one-liter volumetric flask with pure water to prepare a 10^{-3} M MB standard solution. This solution was diluted to the desired concentration before use.

(4) Basic disodium hydrogenphosphate solution. The required quantity of disodium hydrogenphosphate (10.00 g) was dissolved in pure water (*ca.* 800 ml) and the pH of the solution was adjusted to a pH value of 10.0 using a sodium hydroxide solution (4 w/v%), and diluted to the mark of a one-liter volumetric flask with pure water.

Apparatus

The absorbance of solutions was measured by a spectrophotometer (UV-2200; Shimadzu Seisakusho Co. Ltd.) using a cell length of a 10 mm. A shaker was used with 40 mm amplitude and a stroke frequency of 300/min (MS-1; Iuchi Seieido Co. Ltd.).

Procedure

MB spectrophotometry specified in the official standard methods for the determination of AS in tap water was investigated; we found that a rapid and simplified procedure did not lower the accuracy and reproducibility. The proposed method is shown as follows:

A water sample of 50 ml is placed in a separatory funnel; then, 5 ml of a 10^{-3} M MB solution and 5 ml of chloroform are added, and the mixture is shaken for 1 min using a shaker. The separatory funnel is allowed to stand (one minute or less) and the separated chloroform phase is filtered; the absorbance of the chloroform solution is then measured at 654 nm (λ_{max}). The experimental procedure is shown in detail in Fig. 1(a) – (b). Here, the official standard method for the determination of AS in tap water is also described for a reference (Fig. 1(a)).

Results and Discussion

Reaction of DBS and MB

The quilibrium of the DBS, MB and DBS-MB associated ion-pair (DBS-MB ion pair hereafter) in water and

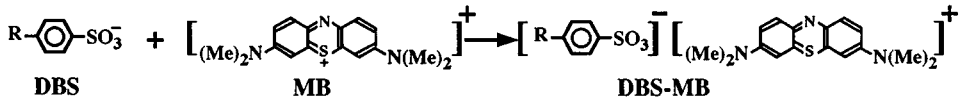

Fig. 2 Reaction scheme of dodecylbenzenesulfonate and Methylene Blue.

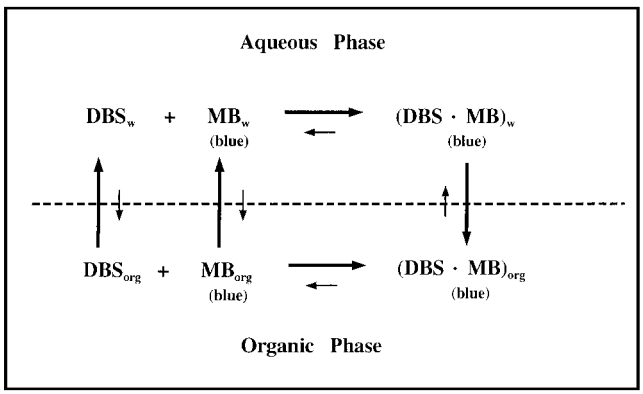

Fig. 3 Equilibrium scheme of DBS and MB in water and chloroform (organic) phases. Note: MB in organic phase is negligible small.

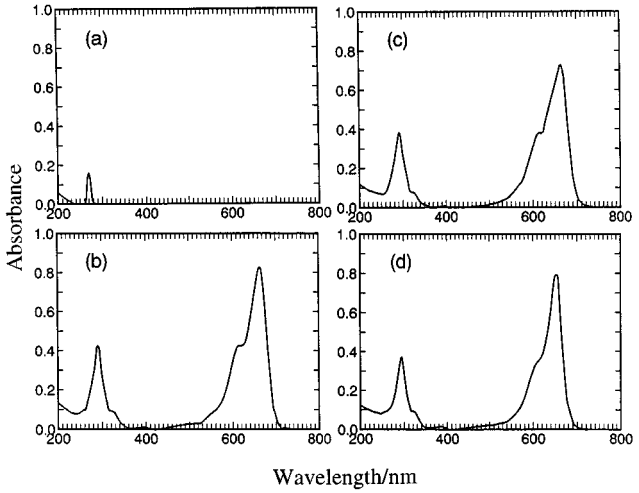

Fig. 4 Absorption spectra of DBS, MB, and DBS-MB associated ion pair in water and chloroform phases. (a) DBS solution in water ([DBS]=1.0×10^{-3} M); (b) MB solution in water ([MB]=1.0×10^{-5} M); (c) DBS+MB mixed solution in water ([DBS]=[MB]=1.0×10^{-5} M); (d) DBS-MS associated ion pair in chloroform ([DBS-MS]=1.0×10^{-5} M).

the chloroform phase were qualitatively investigated. The stability in the respective phase for each species was observed and examined. The DBS dissolved in water was slightly soluble in chloroform. When chloroform was added onto the DBS water solution, it became emulsified. Upon standing, it gradually became clear as time passed, and DBS transferred to the water phase, not to the chloroform phase (absorption spectrum taught these facts). MB dissolved in chloroform (blue color) as well as in water (blue color). However, when water was added into MB chloroform solution, the blue color of the chloroform phase rapidly transferred to the water phase, and after a few seconds of mixing, the color in the chloroform phase disappeared. The fact that the DBS-MB (1:1 molar ratio) associated ion pair in water is easily extracted to the chloroform phase is well known.[7] We have also confirmed the molar ratio of DBS to MB in DBS-MB complex to be 1:1 by the moar ratio method. Reaction scheme of DBS and MB is shown as in Fig. 2. The above mentioned observation shows us that DBS molecules alone in the water phase never transfer to a chloroform phase, but only the associated ion pair of DBS and MB can be extracted to the chloroform phase. Considering these facts, we can draw the equilibrium on these species, as shown in Fig. 3.

Absorption spectra of DBS, MB, and DBS-MB solutions

The absorption spectra of water solutions of a DBS, MB, DBS-MB mixture, and a chloroform solution of DBS-MB associated ion pair are shown in Figs. 4(a) – (d). Figure 4 shows that the absorption spectrum of the DBS-MB ion pair extracted into a chloroform phase is very similar to that of MB, or a DBS-MB mixture (or ion pair?) in a water solution. The absorption maxima of the first (*ca.* 664 nm or 654 nm) and second absorption bands (*ca.* 270 nm) correspond well to each other.

On the other hand, the band spectrum of DBS around 270 nm apparently disappeared in the DBS-MB corresponding band spectrum because of its weak molecular-absorption coefficients. It was found that the DBS-MB ion pair did not give any new band spectrum other than the first and second band spectra. However, the first band of the chloroform phase (654 nm) for the DBS-MB ion pair showed a 10 nm blue shift compared with that of the water phase (664 nm).

Material balance of MB

The absorption maximum of the first band of the MB or DBS-MB mixture (or complex?) in water (664 nm) and that of the DBS-MB ion pair in chloroform (654 nm) were taken into account, and examined the sum of the MB content in water and the MB content out of the DBS-MB ion pair in the chloroform phase. The results are shown in Fig. 5. As shown from the figure, the sum of the MB content in water and the MB content in the chloroform phase are constant (≒100%) in good approximation, although at around DBS/MB ratios of 0.4 – 0.8 the sum of the MB contents in both phases exceeded 100%. The small deviation at around the above-stated region may be due to a volume loss of chloroform into water. As already stated, although MB

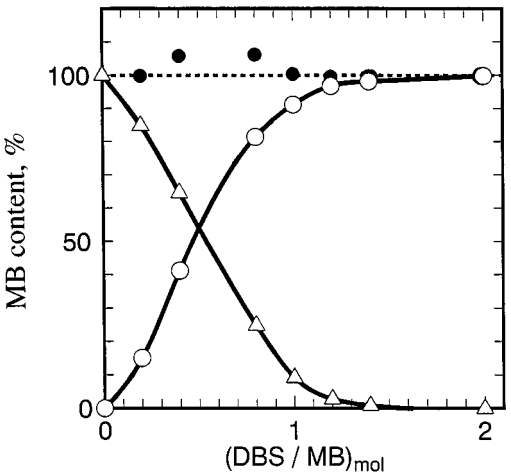

Fig. 5 Relationship between the MB content in water (or MB content in chloroform) and the (DBS/MB) molar ratios. (△) MB content in water phase; (○) MB content in chloroform; (●) sum of MB content in water and chloroform. $[MB]_{mol}$ $=1.0\times10^{-5}$ M (V_{MB}=5.0 ml≡5.0×10^{-8} mol); $([DBS]_{mol}/[MB]_{mol})$ =0.2 – 2.0 molar ratios. The experimental procedure is the same as in the present method, except for the MB concentration.

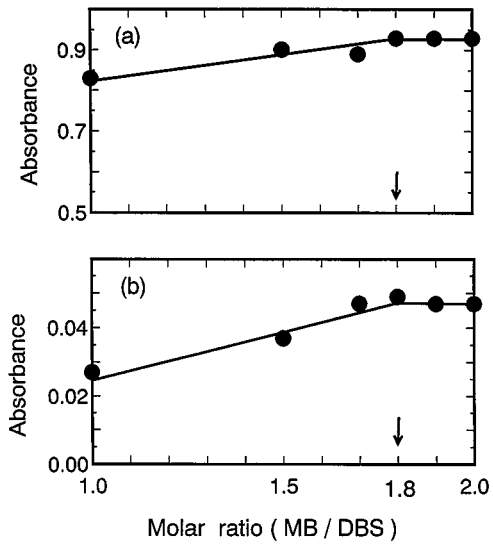

Fig. 6 Least required amount of MB for the determination of DBS. (a): [DBS]=0.7 mg/l (≒2×10^{-6} M); (b): [DBS]=0.03 mg/l (≒8.7×10^{-8} M). The experimental procedures were the same as in the present method, except or the MB concentrations ($[MB]_{mol}/[DBS]_{mol}$=1.0 – 2.0).

in itself dissolves into chloroform, with the addition of water it was swiftly transferred to the water phase, and thus an unreacted or excess amount of MB will exist in the water phase. The DBS-MB ion pair is considered to exists only in the chloroform phase.

Least required quantity of MB to DBS

The concentrations of AS in tap water measured by using the official method ranges from 0.02 to 0.5 mg/l (5.7×10^{-8} – 1.4×10^{-6} M as DBS). According to these values, we chose two concentrations of DBS, *i.e.*, 1×10^{-7} M and 2×10^{-6} M. To determine the least required amount of MB for DBS, the MB concentrations were varied from 1.0 to 2.0 molar ratios the DBS concentrations being fixed ($[MB]/[DBS])_{mol}$=1.0 – 2.0). The experimental procedures were the same as that described in the experimental parts, except for the MB concentrations; also the absorbance was measured to the solution of the extracts from chloroform phase. The results are shown in Fig. 6. This figure shows that at any concentrations of DBS (even at around the lower or upper limit of the concentration) it reaches the maximum absorbance at MB concentrations of 1.8-times or more as high as the DBS concentration (molar ratios). Although it is known that MB and DBS react a 1:1 molar ratio[7] to make an ion pair, it is required twice or more than two-times the MB concentration to that of DBS to make the reaction practically complete. The official method in Japan for tap water uses a MB concentration of 1×10^{-3} M (5×10^{-6} mol absolute), which corresponds to *ca.* 70-times as much as the DBS quantity at the upper-limit concentration of AS (0.5 mg/l≡DBS concentration of 1.4×10^{-6} M≡7×10^{-8} mol absolute). If our experimental results are used, the required MB concentration is *ca.* 3×10^{-5} M (*ca.* 1.5×10^{-7} mol≡absolute value). In the present work, however, we employed a MB solution of 1×10^{-3} M for convenience to compare the official method.

Extraction time

The relationship between the shaking time and the extraction efficiency of the DBS-MB ion pair into chloroform was examined. The experimental conditions were the same as in the present method, except for shaking conditions. Shaking by hand and a machine (shaker) were also compared. The result is shown in Fig. 7. As is obvious from this figure, 30 s shaking is sufficient for both hand-shaking and using a shaker, although 20 s is sufficient for hand-shaking. The shaking time was chosen to be 1 min in the present work for safety purposes.

DBS concentration dependence on extraction efficiencies

The dependence of the DBS concentrations on the extraction efficiencies of the DBS-MB ion pair into the chloroform phase was examined using the proposed method. Perfect extraction efficiencies (100%) were assumed for the official method of AS in tap water. As shown from Fig. 8, the extraction efficiencies were constant (*ca.* 90%) irrespective of the DBS concentrations. Especially, in the DBS concentration range of 0.10 – 0.50 mg/l, the recoveries of the associated complex were stable (RSD=2 – 3%, n=10). As pointed out by Utsumi *et al.*[7], it is not necessary to have perfect extraction efficiencies for the exact determination of surfactants. Reproducible or constant extraction ratios or reproducible calibration curves are most important. To obtain simplified procedures and a shorter operation time, we adopted one-time extraction.

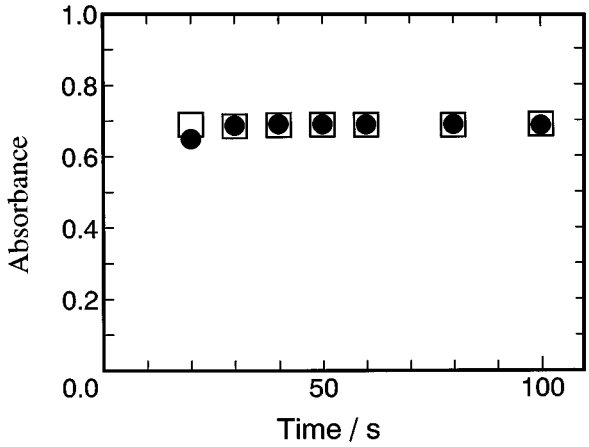

Fig. 7 Effects of the shaking time on the percent extraction of DBS-MB ion pair into the chloroform phase. (□) hand shaking [*ca.* 60 times/min]; ●, machine shaking (shaker) [stroke (4 cm): *ca.* 300 times /min]. The experimental procedures were the same as in the present method, except for the shaking time.

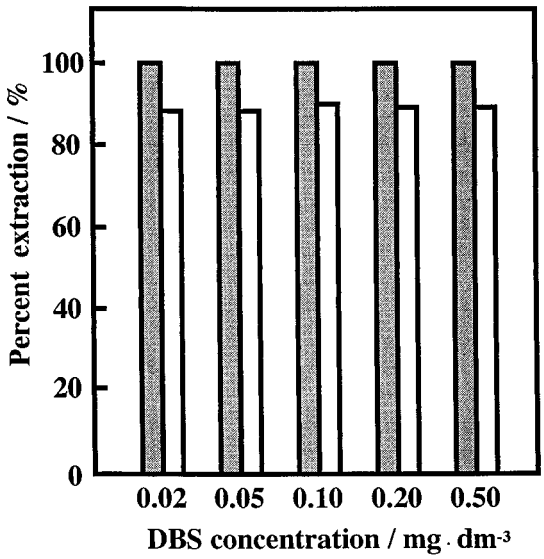

Fig. 8 Relative percent extractions of the DBS-MB ion pair in the present method to the official method (100%). (■) official method (left side); (□) present method (right side); $([MB]/[DBS])_{mol}=10$.

Calibration curve and reproducibility

The calibration curves were made according to the proposed procedures, and a good linear relation was obtained in the DBS concentration range of 5×10^{-8} to 1.5×10^{-6} M (*ca.* 0.02 – 0.5 mg/l)(r=0.9993). As the lower limit, the concentration in the official method for the determination of AS is 0.02 mg/l ($\fallingdotseq5.7\times10^{-8}$ M (as DBS)). The reproducibility of the present method and the official method were thus examined and compared around this concentration. The results are given in Table 1. The standard deviations and relative standard deviations (RSD) obtained for the present (and the official method) were 1.50×10^{-3} (1.45×10^{-3}) mg/l and 7.5%(7.2%), respectively (n=10). The variance of the data was examined for both methods using the F-distribution (F-test; two-tailed) at around the lower-limit concentrations. From the results, equality of the variance was confirmed. For example, around the lower limit concentrations, F=1.07 (experimental values)$<F^{9}_{9}$ (P=0.05 [α=0.025])=4.03 (theoretical). Thus, the difference in the average values was tested using the t-test. A null hypothesis was not rejected, since $t=(\bar{x}_1-\bar{x}_2)/s(\sqrt{(1/n_1+1/n_2)}$ =0.15 (observed)$<t(\phi=18$, $P=\alpha=0.05)=2.10$ (critical). At around the upper-limit concentration, similar experiments was carried out. In this case, a very clear-cut correlation was obtained, *i.e.*, the measured values obtained by the present and the official method agreed very well; the results are also given in Table 1 (RSD=0.64 – 0.65%, n=10).

Thus, the difference in the average values was not meaningful for both methods, and we conclude that both methods have the same accuracy and reproducibility; also, the lower limit (0.02 mg/l) or upper limit (0.05 mg/l) concentration for the improved method are the same as in the official method.

Table 1 Comparison of the official and present methods (mg/l) for the determination of anionic surfactant (DBS) at around the concentrations of the lower limit (0.02 mg/l) and the upper limit (0.50 mg/l)

		Measured value	Average	SD	RSD,%
Lower limit concentration[a]	Official method	0.018, 0.020, 0.022, 0.021, 0.021 0.019, 0.018, 0.020, 0.020, 0.022	0.0201	1.45×10^{-3}	7.2
	Present method	0.020, 0.022, 0.018, 0.019, 0.022 0.020, 0.020, 0.018, 0.019, 0.021	0.0200	1.50×10^{-3}	7.5
Upper limit concentration	Official method	0.502, 0.498, 0.504, 0.500, 0.500 0.506, 0.494, 0.500, 0.502, 0.501	0.5007	3.27×10^{-3}	0.65
	Present method	0.501, 0.503, 0.496, 0.500, 0.495 0.505, 0.500, 0.502, 0.504, 0.500	0.5006	3.20×10^{-3}	0.64

a. At around the lower limit concentrations, $F=(u^2/v^2)=1.07$(observed) < $F(\phi_1=9, \phi_2=9; P=0.05$ [$\alpha=0.025$])=4.03(critical value). $t=(\bar{x}_1-\bar{x}_2)/s(\sqrt{(1/n_1+1/n_2)}=0.15$(observed) < $t(\phi=18, P=0.05)=2.10$(critical value). P=significant level ($\alpha=P/2$=upper probability).

Table 2 Comparison of the official and present methods for the determination of anionic surfactants in practical tap-water samples

Water sample	Official method (mg/l)[a]	(RSD,%)	Present method (mg/l)[a]	(RSD,%)
A	0.017[b]	(15.2)	0.018[b]	(14.3)
B	0.020	(9.6)	0.021	(9.5)
C	0.023	(9.8)	0.024	(10.7)
D	0.028	(10.1)	0.026	(8.8)
E	0.048	(8.6)	0.051	(9.8)
F	0.083	(9.1)	0.081	(7.1)
G	0.104	(7.8)	0.099	(5.7)
H	0.135	(8.3)	0.143	(3.0)
I	0.187	(6.9)	0.193	(5.4)

a. Values described are averaged ones (n=5). Correlation coefficient obtained is, r=0.993.
b. Values described are lower than lower limit concentration.
The lower limit means determination limit, and concentrations are determined within RSD values of *ca*. 10% in the present work.

Application to practical samples

Anionic surfactants in practical tap-water samples were determined using both methods, *i.e*., the present and the official standard method. The results are given in Table 2. As the table shows, both values agreed very well, correlation of both measured values was very high, and the obtained correlation coefficient was 0.993.

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