



Title	Precise estimation of dodecylbenzenesulfonate in aqueous solution containing dissolved organic matter extracted from soil using UV-spectrometry
Author(s)	Hossain, Md. Imam; Ishiguro, Munehide
Citation	European Journal of Soil Science, 73(1), e13150 https://doi.org/10.1111/ejss.13150
Issue Date	2022-01-19
Doc URL	https://hdl.handle.net/2115/87703
Rights	This is the peer reviewed version of the following article: Hossain, M. I., & Ishiguro, M. (2022). Precise estimation of dodecylbenzenesulfonate in aqueous solution containing dissolved organic matter extracted from soil using UV-spectrometry. European Journal of Soil Science, 73(1), e13150 , which has been published in final form at https://doi.org/10.1111/ejss.13150 . This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley' s version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and websites other than Wiley Online Library must be prohibited.
Type	journal article
File Information	Final manuscript.pdf



1 **Precise Estimation of Dodecylbenzenesulfonate (DBS) by**
2 **Using UV-Spectrometry in Aqueous Solution Containing**
3 **Dissolved Organic Matter (DOM) Extracted from Soil**
4

5 Md. Imam Hossain^{a, b *}, Munehide Ishiguro^c

6 ^a *Department of Soil Science, University of Chittagong, Chittagong-4331, Bangladesh*

7 ^b *Graduate School of Agriculture, Hokkaido University, Kita-9, Nishi-9, Kita-ku,*
8 *Sapporo, Japan*

9 ^c *Research Faculty of Agriculture, Hokkaido University, Kita-9, Nishi-9, Kita-ku,*
10 *Sapporo, Japan*

11
12 * **Corresponding author:** Md. Imam Hossain, email: mihossain@cu.ac.bd,
13 Telephone: +81 070 2831 0510
14 Present address: Laboratory of Soil Conservation, Graduate School of Agriculture,
15 Hokkaido University, Kita-9, Nishi-9, Kita-ku, Sapporo, 060-8589, Japan.
16 ORCID: 0000-0003-3801-1701

17
18 **Running Title:** Estimation of DBS from DBS-DOM complex solutions
19

Abstract

Precise estimation of sodium dodecylbenzenesulfonate (DBS) is essential for understanding its adsorption in soils, transport, toxicity, fate, and its application in the remediation of contaminated soil and groundwater. DBS can be easily identified by its conjugated double bond systems of benzene ring under the ultraviolet (UV) spectrum of the spectrophotometer. However, benzene group components of dissolved organic matter (DOM) also absorb light in the UV spectrum, and this effect is responsible for the excess quantities of DBS that are falsely measured by spectrophotometers. This study was conducted to propose a method for accurately measuring the DBS concentration of a solution containing DOM. To elucidate the influence of DOM during the UV-spectroscopic measurement of DBS in an aqueous solution, 222.5 nm UV and 400 nm UV-vis spectra were measured. The DOM was extracted from a highly humic non-allophanic volcanic ash (Andosol) soil by using 1 mmol NaCl/L and 100 mmol NaCl/L solutions as the extractors. The absorbances at both 222.5 nm and 400 nm increased in proportion to the increase in the DOM concentration. The relationship between the absorbances at the two different wavelengths could be expressed as a linear relationship. On the other hand, the absorbance at 400 nm did not increase with the increase in the DBS concentration, while the absorbance at 222.5 nm increased with the increase in the DOM concentration. Therefore, we inferred that the influence of DOM on the absorbance value of the DBS–DOM complex solution at 222.5 nm could be eliminated by using the linear relationship between the two different absorbances of the DBS-free DOM solution. This method makes it possible to easily measure the DBS concentration of a solution from soil water, streams, or industrial effluents containing DOM, without using reagents.

Keywords: Andosol, Dissolved organic matter, dodecylbenzenesulfonate, humic soil, UV-vis, UV Spectrometry.

Highlights

- Dodecylbenzenesulfonate in a solution is overestimated in the presence of dissolved organic matter.
- Dodecylbenzenesulfonate becomes precisely detectable using 222.5 nm and 400 nm spectrophotometry.
- Our proposed method is simple, rapid, efficient, and requires no special reagent or recurring cost.
- This method can be used for precise DBS estimation in soil water, streams, or industrial effluents.

1. Introduction

Nowadays, environmental studies have been largely focused on the presence of surfactants in the soil–water system (Cao et al., 2008; Rodriguez-Escales et al., 2012). Among all the anionic surfactants, dodecyl sulphate and dodecylbenzenesulfonate (DBS) are the ingredients of most currently available cleaning agents and other commonly used commercial products (Myers, 2005; Texter, 1999; Nollet, 2007; Zoller, 2005). Sodium DBS is widely used in industries and households around the globe for the same purpose (Fachini et al., 2007; He et al., 1991; Inoue et al., 1978). However, DBS is also one of the most common organic pollutants found in nearly every environmental component (McAvoy et al., 1994). It is considered as a major soil contaminant and is often present in sewage sludge, solid waste, industrial waste, and wastewater (Sablayrolles et al., 2009).

70 The discharge of DBS into the environment causes it to interact and be adsorbed
71 onto the soil (Ahmed & Ishiguro, 2015). When these compounds are adsorbed onto
72 soils, they appear to degrade slowly (Tabor & Barber, 1996), and are moderately toxic
73 to invertebrates and numerous higher plants (Kloepper-Sams et al., 1996). In fact in the
74 long term, DBS is harmful to aquatic organisms, animals, soils, and plants (Sablayrolles
75 et al., 2009). The use of high amounts of untreated surfactant-contaminated irrigation
76 water is widespread in rural and undeveloped areas. The surfactants can alter soil
77 physicochemical and biological properties (Dai et al., 2001). Anionic surfactants such
78 as DBS are sometimes used as cleaning agents of contaminated soils and groundwater
79 (Mulligan et al., 2001). Therefore, the precise estimation of DBS is essential for
80 understanding its adsorption in soils, transport, toxicity, fate, and its application in the
81 remediation of contaminated soils and groundwater.

82 Dissolved organic matter (DOM) is a major component of organic carbon
83 (Williams et al., 2016) that influences the distribution, mobilization, and degradation
84 of soil pollutants, such as organic toxicants, at the soil- soil solution interface (Chen et
85 al., 2010; Huo et al., 2008; Jiang et al., 2008; Ma et al., 2001; Song et al., 2007).
86 Dissolved organic matter in natural environments consists of diverse types of organic
87 molecules, most of which do not have easily recognizable chemical structure. Besides
88 the non-humic part of the DOM, the maximum portion (50% to 70%) usually covers
89 the humic substances which comprise a general class of biogenic, heterogeneous, and
90 refractory organic compounds, occurring in all terrestrial and aquatic environments
91 (Karavanova, 2013; Pettit, 2008; Thurman, 1985; Wetzel, 1983). Humic substances are
92 significant in hydrochemistry and aquatic toxicology because they can bind both metals
93 and hydrophobic organic pollutants such as DBS (Alberts & Giesy, 1983; Carter &
94 Suffet, 1982; Gjessing & Berglind, 1981; Hassett & Milicic, 1985; Ishiguro & Koopal,

2016; McCarthy & Jimenez, 1985; Servos & Muir, 1989). Usually, humic substances are divided into three different fractions, namely, humic acids, fulvic acids, and humins (Fenchel et al., 2012; Kumada, 1965; Pettit, 2008). Humic acids are dark brown to black in colour, fulvic acids are light yellow to yellow-brown in colour, and humins are black in colour (Stevenson, 1995). Therefore, DOM has a dark yellowish-brown to a black colour appearance in aqueous solution, depending on the quantity and ratio of the different organic portions dissolved in solution (Zhao et al., 2008). It is assumed that the high turbidity of the soil solution is caused by the presence of the DOM, especially when the humic substance is present at a considerably higher quantity. The DOM concentration increases with higher pH, lower electrolyte concentration, and higher anionic surfactant concentration when a highly humic soil was shaken with the solution (Ahmed et al., 2012).

Dodecylbenzenesulfonate concentration in soil solution is sometimes measured by the absorbance of ultraviolet (UV) wavelength with a UV-spectrophotometer (Torn et al., 2003), such as at 222.5 nm, because it allows the detection of the conjugated double bond systems of benzene rings (Nakahara, 2002; Ni et al., 2018). This method is very simple and useful, as the solution could be directly measured without any reagents. However, when DOM is not negligibly included in the solution, DBS concentration must be adjusted, excluding the influence of DOM because the absorbance at the UV spectrum increases with the influence of unsaturated compounds, which includes the benzene ring in the DOM (Zhang et al. 2019). Generally, batch DBS adsorption or desorption experiment of highly humic soils that were previously treated with electrolytes and DBS would display such confusing results under UV-spectroscopy. To eliminate such confusion regarding DBS concentration in the aqueous solution containing a substantial quantity of DOM, it is necessary to precisely measure the

influence of the DOM portion in the solution. Both DBS and DOM absorb the electromagnetic radiation that exhibits a wavelength of 222.5 nm. However, DOM also absorbs visible light with a wavelength of 400 nm, while DBS does not. It is believed that the influence of DOM can be eliminated by using this characteristic.

The aim of this study was to propose a method for the precise estimation of DBS concentration in solutions containing different concentrations of DOM, taking into account the influence of DOM using UV-spectrophotometry. In order to eliminate the influence of DOM, the absorbance at the 400 nm visible light spectrum was measured together with that at the 222.5 nm UV spectrum.

2. Materials and Methods

2.1. Extracted dissolved organic matter solution

To prepare the extracted DOM solution for this study, a highly humic non-allophanic Andosol from the A-horizon (Daisen pasture, Tottori Prefecture, Japan) was used to extract the organic matter. Generally, Andosols have a thick dark A-horizon, with abundant organic matter (Schaetzl & Anderson, 2015). The carbon content of the soil was 13.8%, and the soil physico-chemical characteristics were reported by Ahmed and Ishiguro (2015). The DOM was extracted as dissolved solid (DS) with sodium chloride (NaCl) solution, a method that is almost similar to the salt extraction method of DOM as described by Kalbitz et al. (2007). The extraction was carried out with 1 mmol NaCl/L at pH 6.0 and 100 mmol NaCl/L at pH 5.0, using a soil and electrolyte solution ratio of 1:15 (w/v, dry weight basis) in an electro-mechanical reciprocal shaker at 180 rpm at 25 °C. The pH of the solution was set to a value close to the natural pH at the concentration of the electrolyte solution. Different durations of shaking, namely, 1 h, 6 h, 24 h, and 48 h were applied to different centrifuge tubes to produce DOM

solutions with different concentrations of DS containing DOM. After that, the suspensions were centrifuged at 8000 rpm for 10 min at 25 °C, and, finally, the supernatants were filtered through a No. 6 filter paper and stored in separate plastic bottles.

2.2. Reagents

The principal reagent used in this study was linear sodium DBS, which is an anionic surfactant (Holmberg, 2019) having the chemical composition $C_{12}H_{25}C_6H_4SO_3Na$ and molecular weight of 348.48 g/mol, purchased from Fujifilm Wako Pure Chemical Corporation, Osaka, Japan in white crystalline powder form, with a purity of approximately 99+%. Sodium chloride was also purchased from Fujifilm Wako Pure Chemical Corporation, Osaka, Japan, with a purity of 98+%.

2.3. Dodecylbenzenesulfonate–dissolved organic matter complex solution

To examine the influence of DOM on the DBS solution for the detection of DBS concentration using UV-spectrophotometer, three different concentrations of DBS solutions were prepared. Triplicates of 0, 50, and 500 μmol DBS/L solutions were prepared using the previously extracted DOM solution as a solvent, with eight different concentrations of DS and 1 mmol NaCl/L at pH 6.0 or 100 mmol NaCl/L at pH 5.0. DOM-free DBS solutions were also prepared to obtain the DBS standard curve. After the addition of DBS to the DOM solution, the solution was referred to as the DBS–DOM complex solution, wherein the absorbance characteristics of DBS and DOM overlapped.

2.4. Measurement of absorbance at 222.5 nm and 400 nm

A wavelength of 400 nm is the lowermost wavelength of visible light (400 nm to 780 nm) (Lambert et al., 2014). Given that 400 nm is the visible light wavelength at which the absorbance of humic acid is highest (Kumada, 1965; Sorouradin et al., 1993), this wavelength was adopted in the study. One millilitre of the formerly prepared DBS solutions, from every triplicate, was diluted ten times with deionized water, and the absorbance at 400 nm UV-vis light spectrum and 222.5 nm UV light spectrum were measured using the Shimadzu UV-1208 spectrophotometer. Absorbances both at 222.5 nm and 400 nm for the 10 times-diluted DOM solution without DBS was also recorded along with the DBS standard solutions' calibration curve from the UV-spectrophotometer. Since the original DBS-DOM complex solutions were diluted 10 times before spectroscopic measurements, the NaCl concentrations were 0, 0.1, and 10 mmol/L and the DBS concentrations were 0, 5, and 50 $\mu\text{mol/L}$.

2.5 Dissolved solids concentration

As the DS concentration was supposed to be in proportion to the DOM concentration, the DS concentration was measured as the index of the DOM concentration. The DS concentration of the DOM solution which did not include DBS was measured. After 200 mL of the DOM solution was oven-dried at 60 °C for 4 d, the dry weight was measured, and the DS concentration was calculated.

3. Results

3.1. Influence of dissolved solids and DBS on the absorbance at 222.5 nm

The influence of DS concentrations on the absorbance at 222.5 nm is shown in Fig. 1 and Table 1. The results indicated a strong correlation between the 222.5 nm absorbance and the DS concentration. The absorbance at 222.5 nm increased in

proportion to the DS concentration for both the 0.1 mmol NaCl/L and 10 mmol NaCl/L solutions (Fig. 1).

The absorbance of the DBS–DOM complex solution at 222.5 nm is also plotted in Fig. 1. Similar to the result of DBS-free solution, a strong positive linear relationship at each DBS concentration was found between the absorbance values in the 222.5 nm spectrum and the DS concentration (Table 1). The slopes of the linear lines of the NaCl solutions were similar to those obtained with the different concentrations of DBS solutions; these slope values ranged between 0.021 and 0.022 for 0.1 mmol NaCl/L solutions and went 0.0029 to 0.0033 for 10 mmol NaCl/L solutions (**Table 1**).

3.2. Influence of dissolved solids and DBS on the absorbance at 400 nm

The influences of DS and DBS concentration on absorbance at 400 nm are shown in Fig. 2. The coefficients of determination (R^2) for the 0.1 mmol and 10 mmol NaCl/L solution indicated a strong correlation between the 400 nm absorbance and the DS concentration (Table 1); this absorbance is considered to correspond to the visible DS.

Even if the DBS concentration changed, the absorbance remained constant with constant DS concentration. Therefore, the DBS had no effect on the absorbance at 400 nm, as shown in Fig. 2.

3.3. Relationship between absorbances of the two spectra

The absorbances of the DBS–DOM solutions at 222.5 nm and 400 nm spectra are plotted in Fig. 3. The linear regression lines for the values of the DBS–DOM solution with the same DBS concentration are shown in the figure. A strong linear relationship was observed (Table 1) because the DS concentration was in proportion to the

absorbances at both 222.5 nm (Fig. 1) and 400 nm (Fig. 2). The absorbance at 222.5 nm increased with an increase in absorbance at 400 nm.

The slopes of the linear lines were almost similar among the different concentrations of DBS, and the two NaCl/L solutions (Table 1). For the solution containing 0.1 mmol NaCl/L and 5 μ mol DBS/L, the average increase in the absorbance at 222.5 nm from that at 0 μ mol DBS/L was 0.07, and the standard deviation was 0.005. For the solution containing 0.1 mmol NaCl/L and 50 μ mol DBS/L, the average increase in the absorbance at 222.5 nm was 0.62, and the standard deviation was 0.02. Similarly, the average increase was 0.06 and 0.62, and the standard deviation was 0.002 and 0.008 for the 5 μ mol and 50 μ mol DBS/L solutions, respectively, in 10 mmol NaCl/L solution. The increase in the absorbance at 222.5 nm were almost the same for the solutions with the same DBS concentration, even though the concentration of the NaCl solution differed.

3.4. Elimination of the influence of the dissolved solids on the measurement of DBS concentration

Dodecylbenzenesulfonate had no effect on the absorbance at 400 nm, as shown in Fig. 2. Contrarily, DS concentration showed a strong positive linear relationship with the values in the 400 nm spectra (Fig. 2). It was also found that the 222.5 nm UV-spectrum could detect both DBS and DS in the aqueous solution. Therefore, to overcome and eliminate the aforementioned effects of DS in the aqueous solution during the UV-spectroscopic analysis of DBS, a systematic method could be established using the absorbance values at 222.5 nm and 400 nm.

The two measured spectra showed linear positive increases with an increase in the DS concentration. Therefore, a linear regression model with the absorbance data of

zero-DBS solutions at 222.5 nm and 400 nm, with different DS concentrations, could be used to eliminate the influence of DOM in the DBS–DOM complex solution.

As mentioned, the UV-vis absorbance at 400 nm is positively interrelated to the concentration of DS in the aqueous solution. Measuring the absorbances of the DBS-free DOM solutions with different DS concentrations, at 222.5 nm and 400 nm, a linear regression relationship can be established as follows (**Fig. 3**):

$$y(\text{DOM}) = Ax(\text{DOM}) + B \quad (1)$$

where $y(\text{DOM})$ is the 222.5 nm absorbance of the DBS-free DOM solution, $x(\text{DOM})$ is the 400 nm absorbance of the DBS-free DOM solution, and A and B are constants. The DBS standard curve of absorbance at 222.5 nm versus the DBS concentration is obtained by using the following equation:

$$C = ay(\text{DBS}) + b \quad (2)$$

where C is the DBS concentration, $y(\text{DBS})$ is the 222.5 nm absorbance of the DOM-free DBS solution, and a and b are the constants. The 222.5 nm absorbance for the DBS-DOM complex solution, $y(\text{DBS} + \text{DOM})$, can be written as such because the absorbance is divided into the absorbance value of the DBS, $y(\text{DBS})$, and that of DS, $y(\text{DOM})$, as shown in Fig. 4.

$$y(\text{DBS} + \text{DOM}) = y(\text{DBS}) + y(\text{DOM}). \quad (3)$$

On the other hand, the following equation is satisfied because DBS does not influence the 400 nm absorbance:

$$x(\text{DBS} + \text{DOM}) = x(\text{DOM}) \quad (4)$$

where $x(\text{DBS} + \text{DOM})$ is the 400 nm absorbance of the DBS–DOM complex solution. From equations (1) to (4), we get the DBS concentration of DBS–DOM solution, C,

$$C = a[y(\text{DBS} + \text{DOM}) - \{Ax(\text{DBS} + \text{DOM}) + B\}] + b \quad (5)$$

When $y(\text{DBS}+\text{DOM})$ and $x(\text{DBS}+\text{DOM})$ are measured and the constants, a , b , A , and B are obtained from the standard curves, we can obtain the DBS concentration of DBS–DOM solution by eliminating the influence of DS.

The relationship between the actual and measured DBS concentrations of the DBS–DOM complex solution without elimination of DS influence is shown in Fig. 5. The actual DBS concentration was obtained using appropriately diluted DBS. The measured DBS concentration, shown in Fig. 5, was obtained by directly using the measured 222.5 nm absorbance, $y(\text{DBS}+\text{DOM})$, in Eq. 2 of the DBS standard curve, as follows:

$$C = ay(\text{DBS} + \text{DOM}) + b. \quad (6)$$

The DBS standard curve is also added in the figure. Due to the influence of DS, the measured DBS concentration of the DBS–DOM solution was higher (for both electrolyte conditions) than that of the DOM-free DBS standard solution.

The DBS concentration of the DBS–DOM solution was calculated using Eq. 5. The values of the constants were $a = 79.78$, $b = 1.82$, $A = 5.92$, and $B = 0.072$ for the 0.1 mmol NaCl/L solution and $a = 80.73$, $b = 4.88$, $A = 8.36$, and $B = 0.066$ for the 10 mmol NaCl/L solution. The calculated DBS concentration values, which were almost on the DBS standard curves, are shown in Fig. 6. The effect of DS on the 222.5 nm absorbance was successfully eliminated. The differences in results before and after the DS elimination are evident in Fig. 5.

3.5. Influence of the sodium chloride concentration of the dissolved organic matter-extracted solution on the absorbances

As illustrated in Figs. 1 and 2, the DS concentrations decreased when extracted with higher concentrations of electrolyte solution, (100 mmol NaCl/L) even though the same extraction procedure was followed. The correlations and the slopes of the linear

regression lines between the DS concentration and absorbances at 222.5 nm and 400 nm spectra for 0.1 mmol NaCl/L and 10 mmol NaCl/L conditions are given in **Table 1**. The coefficients of determination (R^2) between DS concentration and absorbance at 222.5 nm and 400 nm for the 0.1 mmol NaCl/L solution were higher than for 10 mmol NaCl/L solution (Figs. 1 and 2). A similar trend was observed for correlations between the absorbances at 222.5 nm and 400 nm spectra.

As shown in Fig. 1 and Table 1, the slope of the DS concentration versus the 222.5 nm absorbance of the 0.1 mmol NaCl/L solution was higher than for the 10 mmol NaCl/L solution. The slope of the DS concentration versus the 400 nm absorbance also showed a similar trend. However, the slope of the linear relationship between 400 nm and 222.5 nm absorbance in the 0.1 mmol NaCl/L solution was different from that for the 10 mmol NaCl/L solution (Fig. 3, Table 1), and the difference was considerably lower.

4. Discussion

We successfully presented a method for the measurement of DBS concentration in the DBS–DOM complex solution by eliminating the effect of DS (Figs. 5 and 6). The exact DBS concentration in the DBS–DOM complex solution was obtained by using its 400 nm absorbance values (Eq. (5)) and the corresponding DOM standard curve (Eq. 1), as well as the 222.5 nm absorbance values of the DBS–DOM complex solution (Eq. 5) and the corresponding DBS standard curve (Eq. 2).

A strong linear correlation between the 222.5 nm absorbance and the DS concentration was observed (**Fig. 1; Table 1**). Although the concentration of DS is not equal to that of the DOM, the DOM concentration is supposed to linearly correlate with the DS concentration from this result because the 222.5 nm absorbance corresponds to the concentration of the unsaturated compounds such as the benzene ring in the DOM

incorporated in the DS solutions. The strong correlation between the 400 nm absorbance and the DS concentration, shown in Fig. 2, suggests that this absorbance corresponds to the visible DS. Since DS concentration corresponds well to DOM concentration, as indicated above, the absorbance at 400 nm also corresponds to the DOM concentration. This shows that we succeeded in eliminating the influence of DOM when measuring the DBS concentration using the proposed method.

The slope of the linear relationship between the DS concentration and the 222.5 nm absorbance of the DBS–DOM complex solution with the same DBS and NaCl concentrations was the same among the solutions with different DBS concentrations (**Fig. 1; Table 1**). The same slope confirms that the absorbance increases in proportion to the increase in DBS concentration, even with the presence of DOM in the solution; that is, the increases in absorbance at 222.5 nm as the DBS concentration increased, were same among the solutions. This also indicates that the NaCl concentration did not affect the increase in absorbance as the DBS concentration increased.

The experimental result provides an insight into the relationship between higher and lower concentrations of electrolyte solutions as the extractant of DOM from soil. A reduction in DS concentration was observed when using the 100 mmol NaCl/L solution as an extractant (Figs. 1 and 2). This was caused by the shielding effect exerted by the higher electrolyte concentration, which weakened the repulsive electrostatic forces among the negatively charged aggregated organic matters in the soil, making it difficult for the DS to dissolve into the solution (Ahmed et al., 2012).

Stronger positive correlations between the DS concentration and the absorbances at 222.5 nm and 400 nm were observed in the present study under lower concentrations of the electrolyte solution (**Fig. 1; Table 1**). It was assumed that the lower DS concentrations at higher NaCl concentrations resulted in a weaker correlation (**Table**

1) due to the decreased accuracy of measurement of smaller DS weights in the case of the higher NaCl concentration. In addition, the higher correlation between the absorbances of two spectra indicates that both absorbances are mainly correlated to DOM concentration, which is supposed to be more accurate than DS concentration (Table 1).

The proportion of the DOM in DS is supposed to differ between the different NaCl concentration values. This might be caused by the difference in the slope (Table 1). As mentioned earlier, due to the shielding effect, DS and DOM dissolution from the soil decreases with an increase in electrolyte concentration. The decrease in DOM is supposed to be larger than DS because the structure of DOM is more flexible, and hydrophobic attraction among humic substances, including DOM, increases with an increase in electrolyte concentration. Therefore, the proportion of DOM in the DS in the DOM solution decreases. The reason for these findings may be the difference in the conformation of the DOM. The structure of DOM shrinks when the electrolyte concentration is larger due to the shielding effect, because the expanding electrostatic force among the charged sites in the DOM molecule is smaller; consequently, this change in conformation might affect the absorbance values. Moreover, the solution pH might affect the DOM conformation, as the electric charge of DOM is pH-dependent (Ghosh and Schnitzer, 1980). Therefore, the DOM standard curve must be prepared under the same solution condition for this measurement. The difference of the slope for the 222.5 nm absorbance vs. 400 nm absorbance was smaller (Table 1). The closer values also indicate that both absorbance values were strongly correlated to the DOM concentration.

As shown in Fig. 5 (b), for the 10 mmol NaCl/L solution, the deviation of the measured 222.5 nm absorption from the standard DBS line, caused by the influence of

368 DOM, was very small due to the lower DS concentration. However, the calculated DBS
369 values for the DBS–DOM complex solution were well adjusted with the proposed
370 method, as shown in Fig. 6 (b). Thus, it can be concluded that the developed method
371 was successfully applied.

372

373

374

5. Conclusions

In the study, we propose a method for the measurement of the DBS concentration of a solution containing DOM by measuring the absorbances at 222.5 nm and 400 nm, without any reagents. The absorbance values at 222.5 nm have been extensively used for DBS measurement because the approach is rather straightforward.

The proposed measurement method is very simple because it involves measurement of absorbance at only two different wavelengths, without the use of any reagents. The DOM is commonly observed in natural waters and soil waters. The DBS concentration of such waters could be easily measured using the proposed method even when the solution includes a non-negligible amount of DOM. Significantly, the method is very effective for the batch DBS adsorption experiment of humic soils because the DOM is dissolved considerably when mixing soil and water. This proposed method could also provide insights into the spectrometric measurement of other organic pollutants, more precisely, in solutions which contain a considerable quantity of DOM. We also consider that our simple, rapid, and reagent-free method characterises a way forward in soil and water pollution chemistry because of the possibility to integrate these algorithms with PC-controlled or stand-alone UV spectrophotometry. This will allow the direct, instant, and precise measurement of DBS from practical environmental samples of natural waters and industrial effluents. However, there is scope for further improvement of the method through investigations with various DOM concentrations from other sources and under different pH conditions.

398 **Acknowledgements**

399 This research was supported by the Japan Society for the Promotion Science (JSPS),
400 Grants-in-Aid for Scientific Research (KAKENHI), with grant number JP18H03963.

401 We would like to thank Editage (www.editage.com) for English language editing. We
402 also thank two anonymous reviewers and EJSS editorial board for their helpful and
403 constructive comments.

404

References

- Ahmed, F., & Ishiguro, M. (2015). Effect of adsorption site potential on adsorption of sodium dodecylbenzenesulfonate in highly humic volcanic ash soil. *Soil Science and Plant Nutrition*, 61(3), 432–439. <https://doi.org/10.1080/00380768.2014.1003144>
- Ahmed, F., Ishiguro, M., & Akae, T. (2012). Dissolution of Humic Substances from Highly Humic Volcanic Ash Soil as Affected by Anionic Surfactant, Electrolyte Concentration and pH. *Journal of Environmental Protection*, 3(3), 280–287. <https://doi.org/10.4236/jep.2012.33035>
- Alberts, J. J., & Giesy, J. P. (1983). Conditional stability constants of trace metals and naturally occurring humic materials: Application in equilibrium models and verification with field data. In R.F. Christman & E. T. Gjessing (Eds.), *Terrestrial and Aquatic Humic Materials* (pp. 333–348). Ann Arbor Science, Ann Arbor.
- Cao, J., Guo, H., Zhu, H. M., Jiang, L., & Yang, H. (2008). Effects of SOM, surfactant and pH on the sorption-desorption and mobility of prometryne in soils. *Chemosphere*, 70(11), 2127–2134. <https://doi.org/10.1016/j.chemosphere.2007.08.062>
- Carter, C. W., & Suffet, I. H. (1982). Binding of DDT to dissolved humic materials. *Environmental Science & Technology*, 16(11), 735–740. <https://doi.org/10.1021/es00105a003>
- Chen, G., Lin, C., Chen, L., & Yang, H. (2010). Effect of size-fractionation dissolved organic matter on the mobility of prometryne in soil. *Chemosphere*, 79(11), 1046–1055. <https://doi.org/10.1016/j.chemosphere.2010.03.038>

429 Dai, S., Liu, G., Qian, Y., & Cheng, X. (2001). The sorption behavior of complex
 430 pollution system composed of aldicarb and surfactant—SDBS. *Water Research*,
 431 35(9), 2286–2290. [https://doi.org/10.1016/S0043-1354\(00\)00491-7](https://doi.org/10.1016/S0043-1354(00)00491-7)

432 Fachini, A., Mendes, M. A., Joekes, I., & Eberlin, M. N. (2007). Oxidation of Sodium
 433 Dodecylbenzenesulfonate with Chrysotile: On-line Monitoring by Membrane
 434 Introduction Mass Spectrometry. *Journal of Surfactants and Detergents*, 10(4),
 435 207–210. <https://doi.org/10.1007/s11743-007-1032-8>

436 Fenchel, T., King, G. M., & Blackburn, T. H. (2012). Chapter 3—Degradation of
 437 Organic Polymers and Hydrocarbons. In T. Fenchel, G. M. King, & T. H.
 438 Blackburn (Eds.), *Bacterial Biogeochemistry (Third Edition)* (3rd ed., pp. 49–
 439 57). Academic Press. <https://doi.org/10.1016/B978-0-12-415836-8.00003-7>

440 Ghosh, K., & Schnitzer, M. (1980). Macromolecular structure of humic substances. *Soil*
 441 *Sci.*, 129, 266-276.

442 Gjessing, E. T., & Berglind, L. (1981). Adsorption of PAH to Aquatic Humus. *Arch.*
 443 *Hydrobiol.*, 92(1), 24–30.

444 Hassett, J. P., & Milicic, Edwina. (1985). Determination of equilibrium and rate
 445 constants for binding of a polychlorinated biphenyl congener by dissolved
 446 humic substances. *Environmental Science & Technology*, 19(7), 638–643.
 447 <https://doi.org/10.1021/es00137a010>

448 He, W. S., Wang, R. F., & Chen, J. J. (1991). Erythrocyte Micronucleus of Tadpole
 449 (*Bufo bufo* Andrews) by Synthetic Detergent Powder. *Acta Scientiae*
 450 *Curcumstaniae*, 11(3), 351–357.

451 Holmberg, K. (2019). Surfactants. In *Ullmann's Encyclopedia of Industrial Chemistry*
 452 (pp. 1–56). American Cancer Society.
 453 https://doi.org/10.1002/14356007.a25_747.pub2

454 Huo, S., Xi, B., Yu, H., He, L., Fan, S., & Liu, H. (2008). Characteristics of dissolved
 455 organic matter (DOM) in leachate with different landfill ages. *Journal of*
 456 *Environmental Sciences*, 20(4), 492–498. [https://doi.org/10.1016/S1001-](https://doi.org/10.1016/S1001-0742(08)62085-9)
 457 0742(08)62085-9

458 Inoue, K., Kaneko, K., & Yoshida, M. (1978). Adsorption of dodecylbenzenesulfonates
 459 by soil colloids and influence of soil colloids on their degradation. *Soil Science*
 460 *and Plant Nutrition*, 24(1), 91–102.
 461 <https://doi.org/10.1080/00380768.1978.10433082>

462 Ishiguro, M., & Koopal, L. K. (2016). Surfactant adsorption to soil components and
 463 soils. *Advances in Colloid and Interface Science*, 231, 59—102.
 464 <https://doi.org/10.1016/j.cis.2016.01.006>

465 Jiang, L., Huang, J., Liang, L., Zheng, P. Y., & Yang, H. (2008). Mobility of
 466 Prometryne in Soil As Affected by Dissolved Organic Matter. *J. Agric. Food*
 467 *Chem.*, 56(24), 11933–11940. <https://doi.org/10.1021/jf8023134>

468 Kalbitz, K., Angers, D., Kaiser, K., & Chantigny, M. (2007). Extraction and
 469 Characterization of Dissolved Organic Matter. In M. Carter & E. Gregorich
 470 (Eds.), *Soil Sampling and Methods of Analysis, Second Edition*. CRC Press.
 471 <https://doi.org/10.1201/9781420005271.ch48>

472 Karavanova, E. I. (2013). Dissolved organic matter: Fractional composition and
 473 sorbability by the soil solid phase (Review of literature). *Eurasian Soil Science*,
 474 46(8), 833–844. <https://doi.org/10.1134/S1064229313080048>

475 Kloepper-Sams, P., Torfs, F., Feijtel, T., & Gooch, J. (1996). Effects assessments for
 476 surfactants in sludge-amended soils: A literature review and perspectives for
 477 terrestrial risk assessment. *Science of The Total Environment*, 185(1), 171–185.
 478 [https://doi.org/10.1016/0048-9697\(95\)05050-7](https://doi.org/10.1016/0048-9697(95)05050-7)

479 Kumada, K. (1965). Studies on the colour of humic acids. *Soil Science and Plant*
 480 *Nutrition*, 11(4), 11–16. <https://doi.org/10.1080/00380768.1965.10433805>

481 Lambert, J. B., Shurvell, H. F., Lightner, D. A., & Cooks, R. G. (2014). *Organic*
 482 *Structural Spectroscopy* (2nd ed.). Pearson Education Limited.

483 Ma, H., Allen, H. E., & Yin, Y. (2001). Characterization of isolated fractions of
 484 dissolved organic matter from natural waters and a wastewater effluent. *Water*
 485 *Research*, 35(4), 985–996. [https://doi.org/10.1016/S0043-1354\(00\)00350-X](https://doi.org/10.1016/S0043-1354(00)00350-X)

486 McAvoy, D. C., White, C. E., Moore, B. L., & Rapaport, R. A. (1994). Chemical fate
 487 and transport in a domestic septic system: Sorption and transport of anionic and
 488 cationic surfactants. *Environmental Toxicology and Chemistry*, 13(2), 213–221.
 489 <https://doi.org/10.1002/etc.5620130205>

490 McCarthy, J. F., & Jimenez, B. D. (1985). Interactions between polycyclic aromatic
 491 hydrocarbons and dissolved humic material: Binding and dissociation.
 492 *Environmental Science & Technology*, 19(11), 1072–1076.
 493 <https://doi.org/10.1021/es00141a008>

494 Mulligan, C. N., Yong, R. N., & Gibbs, B. F. (2001). Surfactant-enhanced
 495 remediation of contaminated soil: A review. *Engineering Geology*, 60(1),
 496 371–380. [https://doi.org/10.1016/S0013-7952\(00\)00117-4](https://doi.org/10.1016/S0013-7952(00)00117-4)

497 Myers, D. (2005). *Surfactant Science and Technology: Third Edition*.
 498 <https://doi.org/10.1002/047174607X>

499 Nakahara, M. (2002). *The Science of Color*. Baifukan Publication.

500 Ni, X., Li, Z., & Wang, Y. (2018). Adsorption Characteristics of Anionic Surfactant
 501 Sodium Dodecylbenzene Sulfonate on the Surface of Montmorillonite
 502 Minerals. *Frontiers in Chemistry*, 6, 390.
 503 <https://doi.org/10.3389/fchem.2018.00390>

504 Nollet, B. T. and L. M. L. (2007). Analysis of Surfactants in Samples from the Aquatic
 505 Environment. In *Handbook of Water Analysis* (2nd ed.). CRC Press.
 506 Pettit, R. (2008). *Organic matter, Humus, Humate, Humic acid, Fulvic acid*.
 507 <https://humates.com/wp-content/uploads/2020/04/ORGANICMATTERPettit.pdf>
 508 Rodriguez-Escales, P., Sayara, T., Vicent, T., & Folch, A. (2012). Influence of soil
 509 granulometry on pyrene desorption in groundwater using surfactants. *Water,*
 510 *Air, and Soil Pollution*, 223(1), 125–133. [https://doi.org/10.1007/s11270-011-](https://doi.org/10.1007/s11270-011-0844-3)
 511 [0844-3](https://doi.org/10.1007/s11270-011-0844-3)
 512 Sablayrolles, C., Montréjaud-Vignoles, M., Silvestre, J., & Treilhou, M. (2009). Trace
 513 Determination of Linear Alkylbenzene Sulfonates: Application in Artificially
 514 Polluted Soil—Carrots System. *International Journal of Analytical Chemistry*,
 515 2009, 404836. <https://doi.org/10.1155/2009/404836>
 516 Schaetzel, R. J., & Anderson, S. (2015). *Soils-Genesis and Geomorphology*
 517 *(Hardcover)* ; 9780521812016 ; *Soil science, sedimentology, Soils: Genesis*.
 518 Servos, M. R., & Muir, D. C. G. (1989). Effect of dissolved organic matter from
 519 Canadian shield lakes on the bioavailability of 1,3,6,8-Tetrachlorodibenzo-p-
 520 dioxin to the amphipod *Crangonyx laurentianus*. *Environmental Toxicology and*
 521 *Chemistry*, 8(2), 141–150. <https://doi.org/10.1002/etc.5620080205>
 522 Song, N. H., Yin, X. L., Chen, G. F., & Yang, H. (2007). Biological responses of wheat
 523 (*Triticum aestivum*) plants to the herbicide chlorotoluron in soils.
 524 *Chemosphere*, 68(9), 1779–1787.
 525 <https://doi.org/10.1016/j.chemosphere.2007.03.023>
 526 Sorouradin, M.-H., Hiraide, M., & Kawaguchi, H. (1993). Spectrophotometric
 527 Determination of Humic Substances in Water by Sorption on XAD-2 Resin
 528 Followed by Desorption with Sodium Dodecyl Sulfate. *Analytical Sciences*,
 529 9(6), 863–865. <https://doi.org/10.2116/analsci.9.863>

530 Stevenson, F. J. (1995). *Humus Chemistry: Genesis, Composition, Reactions* (Second
531 Edition, Vol. 72). Wiley. <https://doi.org/10.1021/ed072pA93.6>

532 Tabor, C. F., & Barber, L. B. (1996). Fate of Linear Alkylbenzene Sulfonate in the
533 Mississippi River. *Environmental Science & Technology*, 30(1), 161–171.
534 <https://doi.org/10.1021/es950210p>

535 Texter, J. (1999). *Characterization of Surfactants- Surfactants A Practical Handbook*
536 (K.R. Lange, Ed.). Hanser Gardner Publications Inc.

537 Thurman, E. M. (1985). *Organic geochemistry of natural waters*. Kluwer Academic.

538 Torn, L. H., Keizer, A. de, Koopal, L. K., & Lyklema, J. (2003). Mixed adsorption of
539 poly(vinylpyrrolidone) and sodium dodecylbenzenesulfonate on kaolinite.
540 *Journal of Colloid and Interface Science*, 260(1), 2.
541 [https://doi.org/10.1016/S0021-9797\(03\)00046-8](https://doi.org/10.1016/S0021-9797(03)00046-8)

542 Wetzel, R. G. (Ed.). (1983). Organic carbon cycling and detritus. In *Limnology (Edited*
543 *by R.G. Wetzel)* (2nd Edition, pp. 667–706). Saunders Co.

544 Williams, J. S., Dungait, J. A. J., Bol, R., & Abbott, G. D. (2016). Comparison of
545 extraction efficiencies for water-transportable phenols from different land uses.
546 *Organic Geochemistry*, 102, 45–51.
547 <https://doi.org/10.1016/j.orggeochem.2016.09.010>

548 Zhang, Hanbing, Yue Li, Mingyue Pang, Min Xi, and Fanlong Kong. 2019. “Responses
549 of Contents and Structure of DOM to *Spartina Alterniflora* Invasion in Yanghe
550 Estuary Wetland of Jiaozhou Bay, China.” *Wetlands* 39(4):729–41. doi:
551 10.1007/s13157-019-01124-3.

552 Zhao, L., Luo, F., Wasikiewicz, J. M., Mitomo, H., Nagasawa, N., Yagi, T., Tamada,
553 M., & Yoshii, F. (2008). Adsorption of humic acid from aqueous solution onto

554 irradiation-crosslinked carboxymethylchitosan. *Bioresource Technology*, 99(6),
555 1911–1917. <https://doi.org/10.1016/j.biortech.2007.03.030>
556 Zoller, U. (2005). *Handbook of Detergents, Part C: Analysis* (Vol. 123). Marcel
557 Dekker. 10.1021/ja0410340
558

559 **Table 1:** The coefficient of determination (R^2) and slope range from the regression
560 analyses between dissolved solid (DS) concentration and absorbances (Abs.) at 222.5
561 nm and 400 nm spectra for 0.1 mmol NaCl/L and 10 mmol NaCl/L conditions
562 (summarized from Figure 1, 2, and 3).

Regression between	R^2 range (Min.–Max.)		Slope range (Min.–Max.)	
	0.1 mmol NaCl/L	10 mmol NaCl/L	0.1 mmol NaCl/L	10 mmol NaCl/L
DS conc. vs. Abs. at 222.5 nm	0.992–0.995	0.398–0.917	0.021–0.022	0.0029–0.0033
DS conc. vs. Abs. at 400 nm	0.986–0.989	0.807–0.896	0.0036–0.0037	0.00036–0.00037
Abs. at 222.5 nm vs. Abs. at 400 nm	0.989–0.997	0.661–0.949	5.9	7.8–9.8

563

564

565

FIGURE CAPTIONS

Figure 1: Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations on the 222.5 nm spectrum for the 0.1 mmol NaCl/L and 10 mmol NaCl/L conditions.

Figure 2: Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations on the 400 nm spectrum for the 0.1 mmol NaCl/L and 10 mmol NaCl/L conditions.

Figure 3: Relationships between the absorbance at 222.5 nm and 400 nm UV-vis spectra measured with respect to the dodecylbenzenesulfonate (DBS) concentration in the 0.1 mmol NaCl/L and 10 mmol NaCl/L solutions.

Figure 4: Linear regression relationships established from the absorbance values at 222.5 nm and 400 nm to eliminate the influence of dissolved solids (DS) in the dodecylbenzenesulfonate (DBS)–DOM complex solutions.

Figure 5: Relationship between the actual and measured dodecylbenzenesulfonate (DBS) concentrations for DBS–DOM complex solutions with **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L before the elimination of the influence of dissolved solids (DS). The dotted line is the standard DBS curve.

Figure 6: The calculated dodecylbenzenesulfonate (DBS) concentration compared to the respective actual values for the DBS–DOM complex solutions with **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L after the elimination of the influence of dissolved solids (DS). The dotted line is the standard DBS curve.

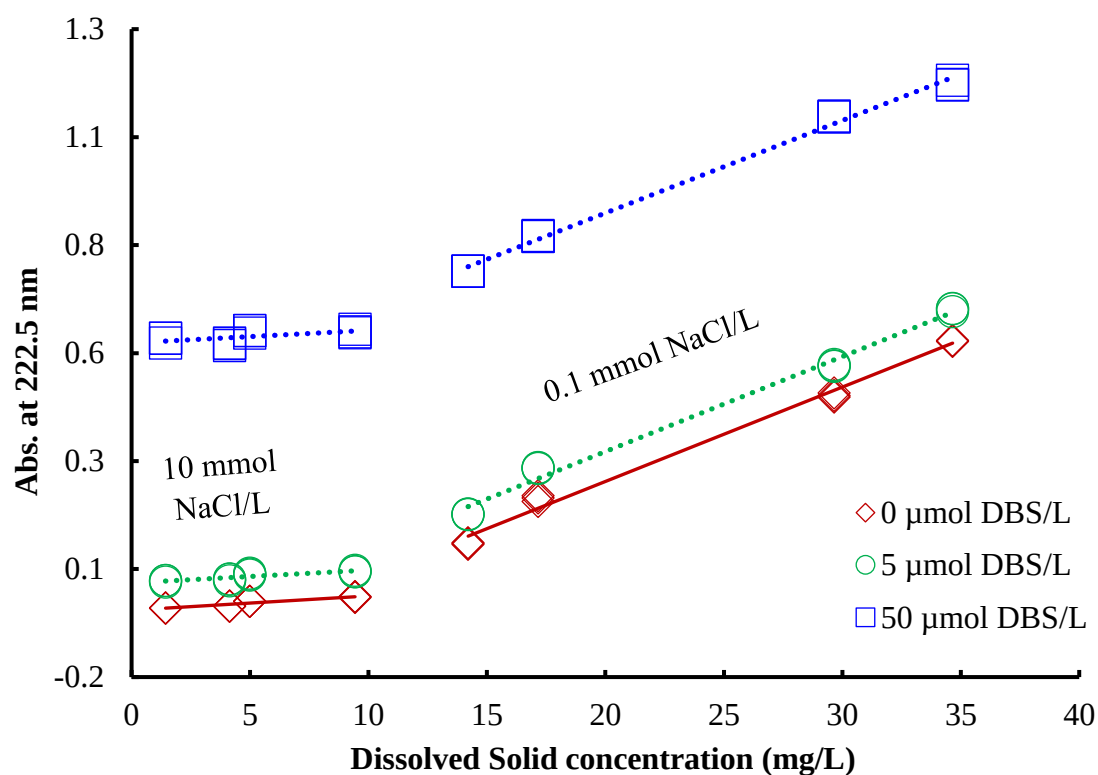


Figure 1: Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations on the 222.5 nm spectrum for the 0.1 mmol NaCl/L and 10 mmol NaCl/L conditions.

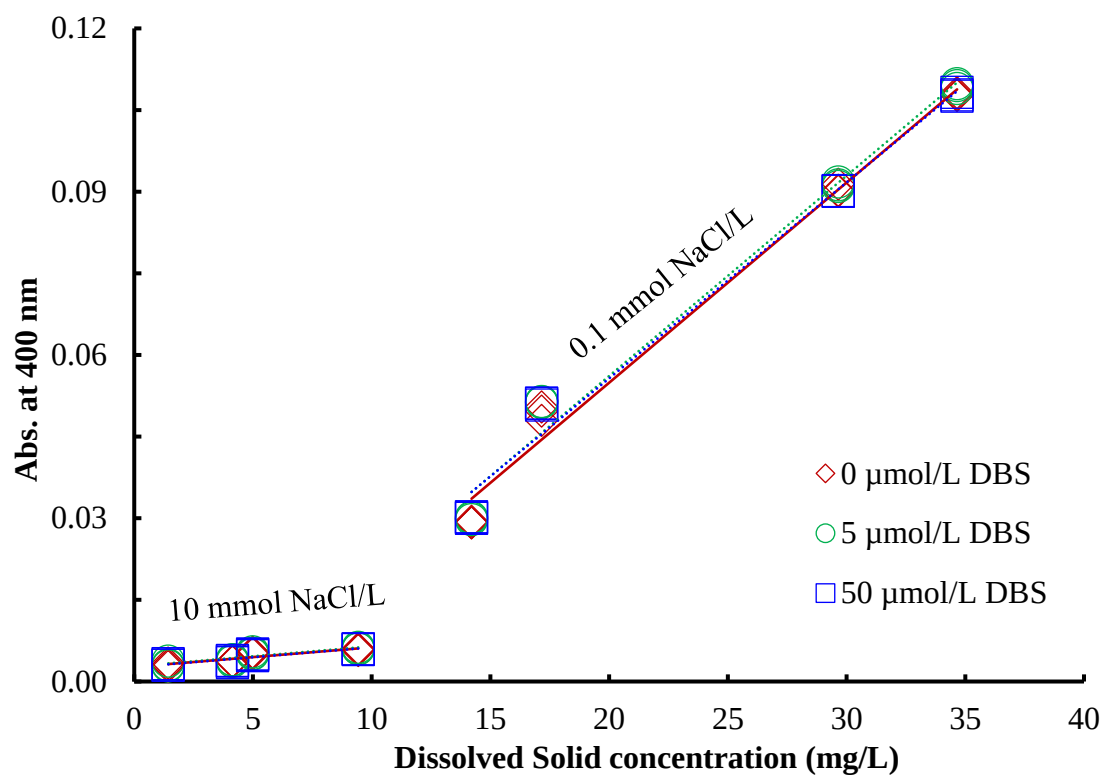


Figure 2: Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations on the 400 nm spectrum for the 0.1 mmol NaCl/L and 10 mmol NaCl/L conditions.

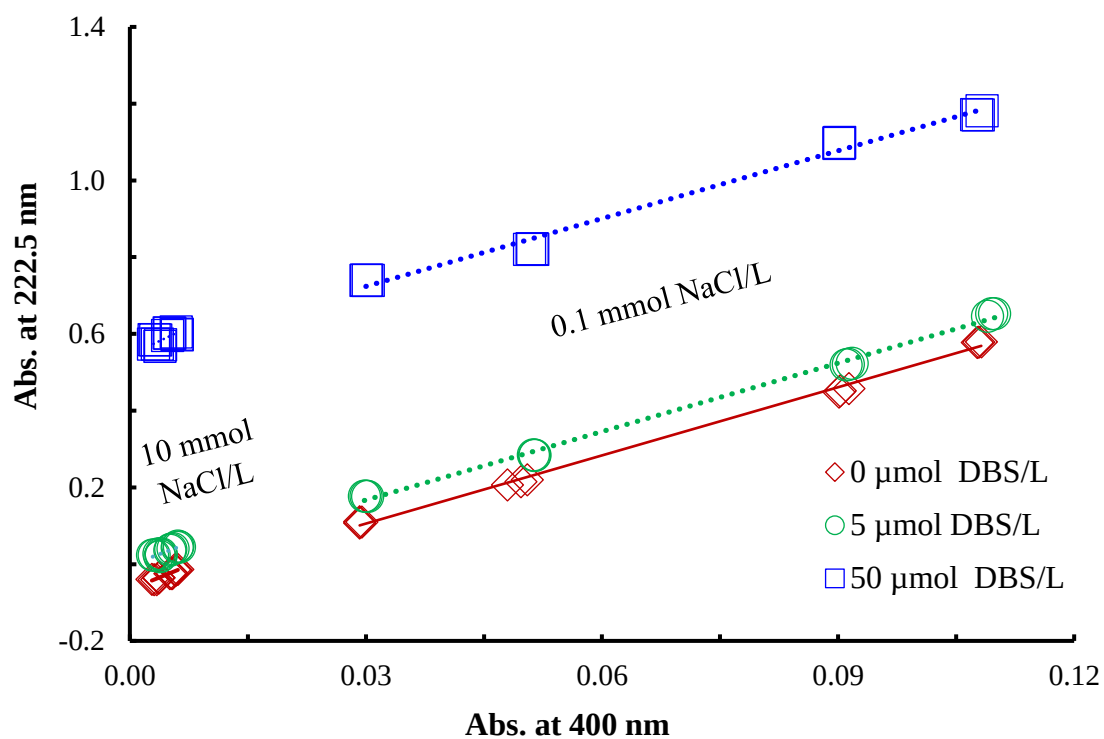


Figure 3: Relationships between the absorbance at 222.5 nm and 400 nm UV-vis spectra measured with respect to the dodecylbenzenesulfonate (DBS) concentration in the 0.1 mmol NaCl/L and 10 mmol NaCl/L solutions.

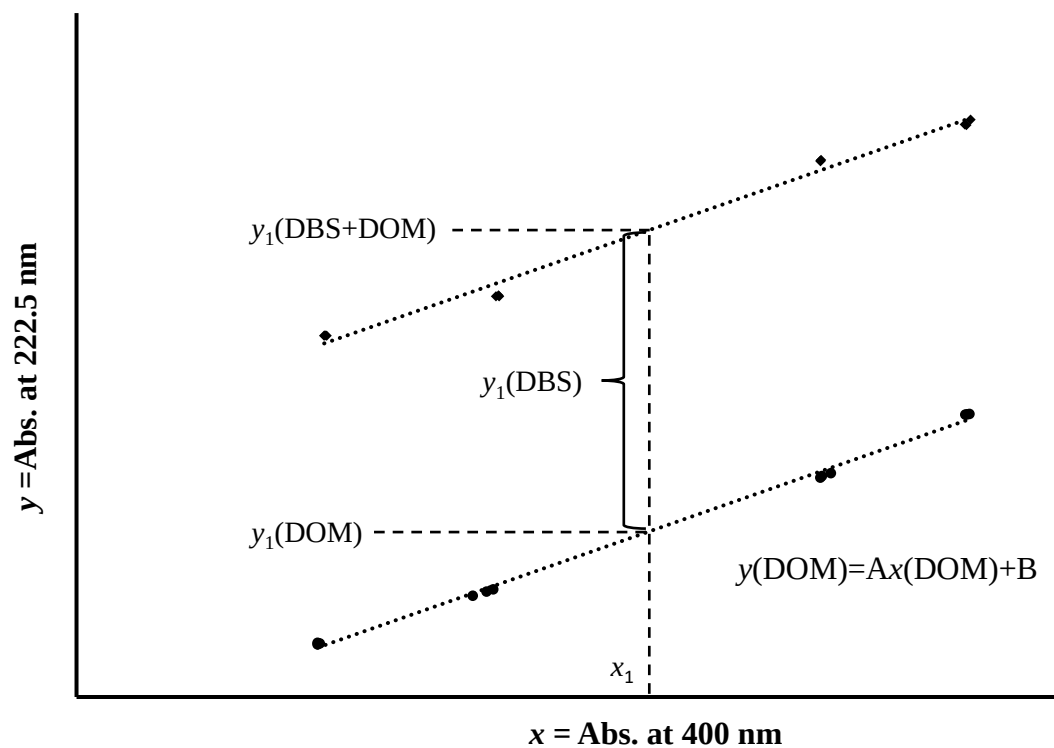


Figure 4: Linear regression relationships established from the absorbance values at 222.5 nm and 400 nm to eliminate the influence of dissolved solids (DS) in the dodecylbenzenesulfonate (DBS)–DOM complex solutions.

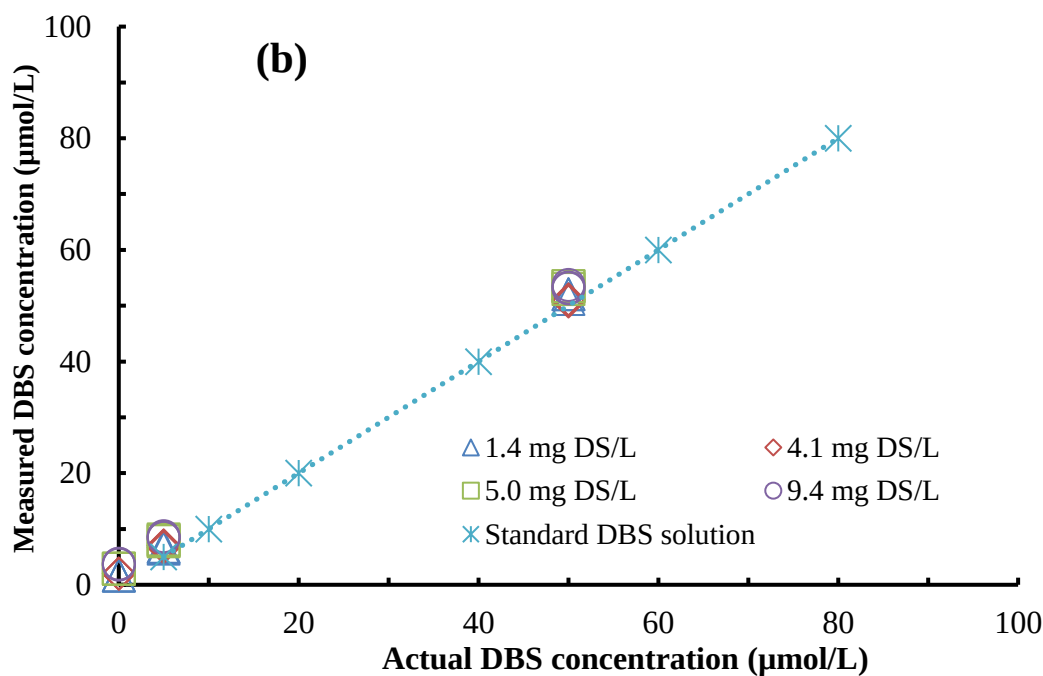
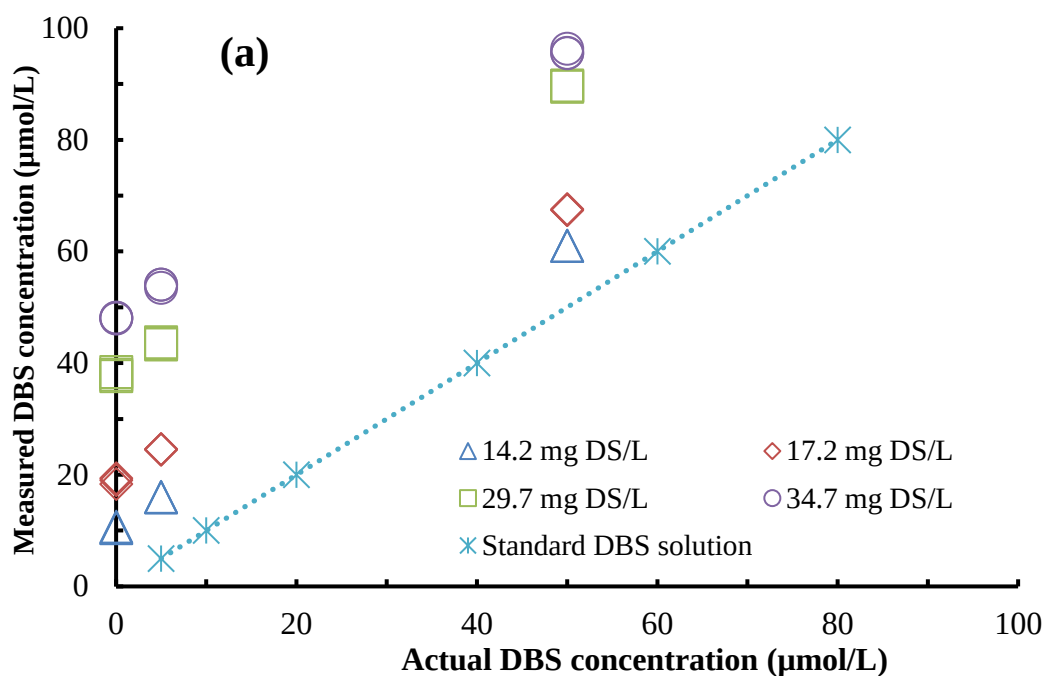


Figure 5: Relationship between the actual and measured dodecylbenzenesulfonate (DBS) concentrations for DBS–DOM complex solutions with **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L before the elimination of the influence of dissolved solids (DS). The dotted line is the standard DBS curve.

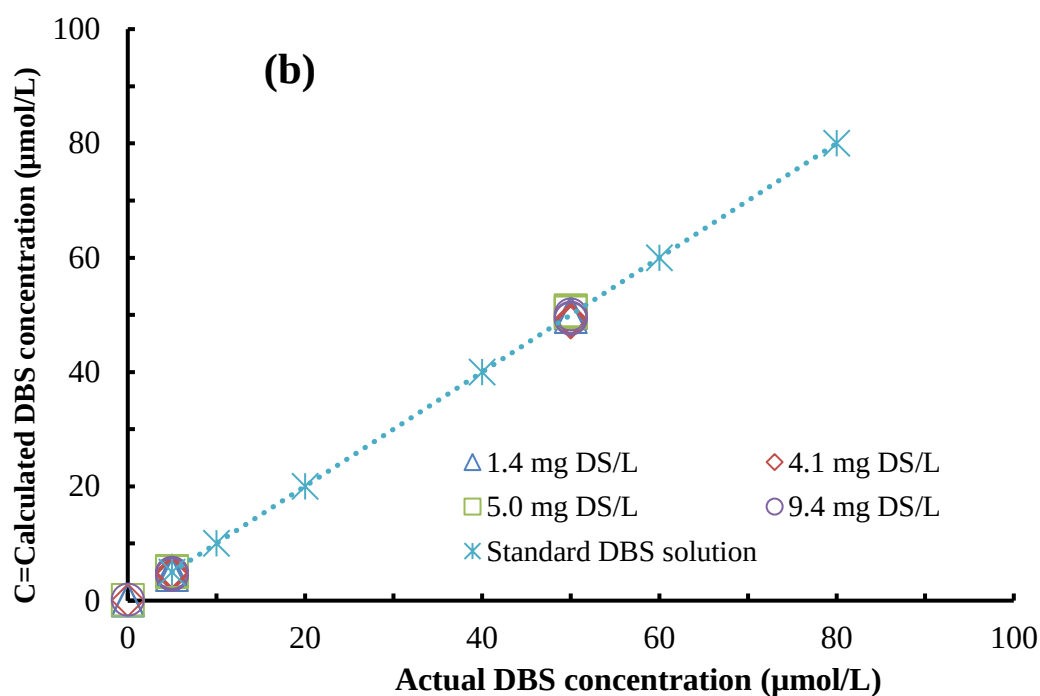
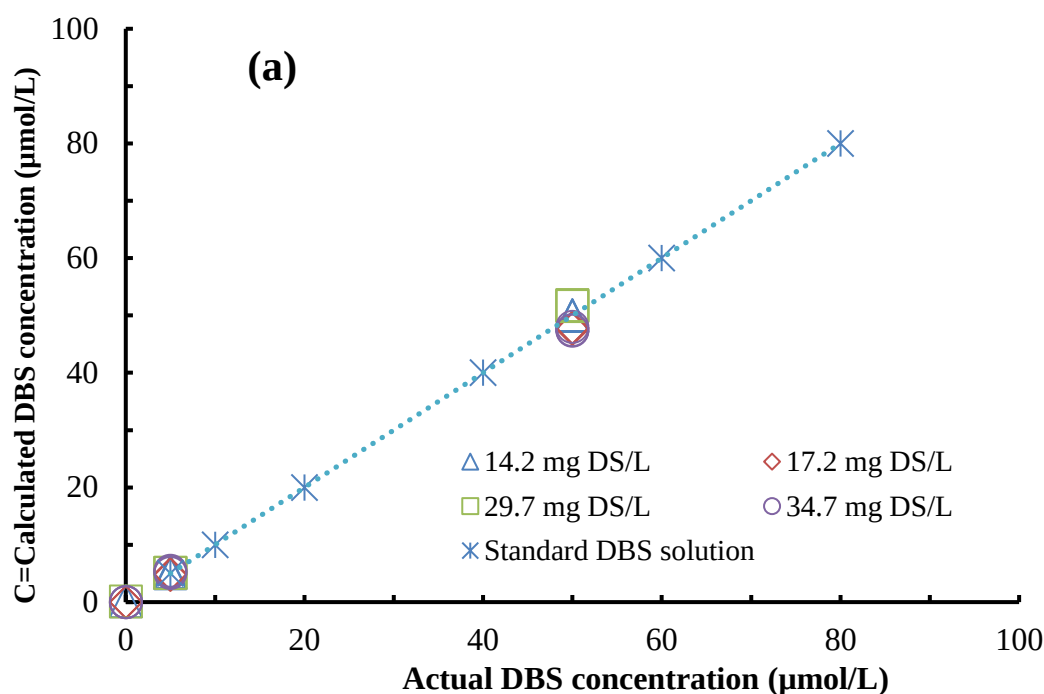


Figure 6: The calculated dodecylbenzenesulfonate (DBS) concentration compared to the respective actual values for the DBS–DOM complex solutions with **(a)** 0.1 mmol NaCl/L and **(b)** 10 mmol NaCl/L after the elimination of the influence of dissolved solids (DS). The dotted line is the standard DBS curve.