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

4

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17

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

19

20 **Abstract**

21 Precise estimation of sodium dodecylbenzenesulfonate (DBS) is essential for  
22 understanding its adsorption in soils, transport, toxicity, fate, and its application in the  
23 remediation of contaminated soil and groundwater. DBS can be easily identified by its  
24 conjugated double bond systems of benzene ring under the ultraviolet (UV) spectrum  
25 of the spectrophotometer. However, benzene group components of dissolved organic  
26 matter (DOM) also absorb light in the UV spectrum, and this effect is responsible for  
27 the excess quantities of DBS that are falsely measured by spectrophotometers. This  
28 study was conducted to propose a method for accurately measuring the DBS  
29 concentration of a solution containing DOM. To elucidate the influence of DOM during  
30 the UV-spectroscopic measurement of DBS in an aqueous solution, 222.5 nm UV and  
31 400 nm UV-vis spectra were measured. The DOM was extracted from a highly humic  
32 non-allophanic volcanic ash (Andosol) soil by using 1 mmol NaCl/L and 100 mmol  
33 NaCl/L solutions as the extractors. The absorbances at both 222.5 nm and 400 nm  
34 increased in proportion to the increase in the DOM concentration. The relationship  
35 between the absorbances at the two different wavelengths could be expressed as a linear  
36 relationship. On the other hand, the absorbance at 400 nm did not increase with the  
37 increase in the DBS concentration, while the absorbance at 222.5 nm increased with the  
38 increase in the DOM concentration. Therefore, we inferred that the influence of DOM  
39 on the absorbance value of the DBS–DOM complex solution at 222.5 nm could be  
40 eliminated by using the linear relationship between the two different absorbances of the  
41 DBS-free DOM solution. This method makes it possible to easily measure the DBS  
42 concentration of a solution from soil water, streams, or industrial effluents containing  
43 DOM, without using reagents.

44

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

47

## 48 **Highlights**

49 ● Dodecylbenzenesulfonate in a solution is overestimated in the presence of dissolved  
50 organic matter.

51 ● Dodecylbenzenesulfonate becomes precisely detectable using 222.5 nm and 400 nm  
52 spectrophotometry.

53 ● Our proposed method is simple, rapid, efficient, and requires no special reagent or  
54 recurring cost.

55 ● This method can be used for precise DBS estimation in soil water, streams, or  
56 industrial effluents.

57

## 58 **1. Introduction**

59 Nowadays, environmental studies have been largely focused on the presence of  
60 surfactants in the soil–water system (Cao et al., 2008; Rodriguez-Escales et al., 2012).  
61 Among all the anionic surfactants, dodecyl sulphate and dodecylbenzenesulfonate  
62 (DBS) are the ingredients of most currently available cleaning agents and other  
63 commonly used commercial products (Myers, 2005; Texter, 1999; Nollet, 2007; Zoller,  
64 2005). Sodium DBS is widely used in industries and households around the globe for  
65 the same purpose (Fachini et al., 2007; He et al., 1991; Inoue et al., 1978). However,  
66 DBS is also one of the most common organic pollutants found in nearly every  
67 environmental component (McAvoy et al., 1994). It is considered as a major soil  
68 contaminant and is often present in sewage sludge, solid waste, industrial waste, and  
69 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,

95 2016; McCarthy & Jimenez, 1985; Servos & Muir, 1989). Usually, humic substances  
96 are divided into three different fractions, namely, humic acids, fulvic acids, and humins  
97 (Fenchel et al., 2012; Kumada, 1965; Pettit, 2008). Humic acids are dark brown to black  
98 in colour, fulvic acids are light yellow to yellow-brown in colour, and humins are black  
99 in colour (Stevenson, 1995). Therefore, DOM has a dark yellowish-brown to a black  
100 colour appearance in aqueous solution, depending on the quantity and ratio of the  
101 different organic portions dissolved in solution (Zhao et al., 2008). It is assumed that  
102 the high turbidity of the soil solution is caused by the presence of the DOM, especially  
103 when the humic substance is present at a considerably higher quantity. The DOM  
104 concentration increases with higher pH, lower electrolyte concentration, and higher  
105 anionic surfactant concentration when a highly humic soil was shaken with the solution  
106 (Ahmed et al., 2012).

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

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

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

129

## 130 **2. Materials and Methods**

### 131 *2.1. Extracted dissolved organic matter solution*

132 To prepare the extracted DOM solution for this study, a highly humic non-  
133 allophanic Andosol from the A-horizon (Daisen pasture, Tottori Prefecture, Japan) was  
134 used to extract the organic matter. Generally, Andosols have a thick dark A-horizon,  
135 with abundant organic matter (Schaetzl & Anderson, 2015). The carbon content of the  
136 soil was 13.8%, and the soil physico-chemical characteristics were reported by Ahmed  
137 and Ishiguro (2015). The DOM was extracted as dissolved solid (DS) with sodium  
138 chloride (NaCl) solution, a method that is almost similar to the salt extraction method  
139 of DOM as described by Kalbitz et al. (2007). The extraction was carried out with 1  
140 mmol NaCl/L at pH 6.0 and 100 mmol NaCl/L at pH 5.0, using a soil and electrolyte  
141 solution ratio of 1:15 (w/v, dry weight basis) in an electro-mechanical reciprocal shaker  
142 at 180 rpm at 25 °C. The pH of the solution was set to a value close to the natural pH  
143 at the concentration of the electrolyte solution. Different durations of shaking, namely,  
144 1 h, 6 h, 24 h, and 48 h were applied to different centrifuge tubes to produce DOM

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

149

## 150 *2.2. Reagents*

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

157

## 158 *2.3. Dodecylbenzenesulfonate–dissolved organic matter complex solution*

159 To examine the influence of DOM on the DBS solution for the detection of DBS  
160 concentration using UV-spectrophotometer, three different concentrations of DBS  
161 solutions were prepared. Triplicates of 0, 50, and 500  $\mu\text{mol}$  DBS/L solutions were  
162 prepared using the previously extracted DOM solution as a solvent, with eight different  
163 concentrations of DS and 1 mmol NaCl/L at pH 6.0 or 100 mmol NaCl/L at pH 5.0.  
164 DOM-free DBS solutions were also prepared to obtain the DBS standard curve. After  
165 the addition of DBS to the DOM solution, the solution was referred to as the DBS–  
166 DOM complex solution, wherein the absorbance characteristics of DBS and DOM  
167 overlapped.

168

## 169 *2.4. Measurement of absorbance at 222.5 nm and 400 nm*



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

182

### 183 *2.5 Dissolved solids concentration*

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

189

## 190 **3. Results**

### 191 *3.1. Influence of dissolved solids and DBS on the absorbance at 222.5 nm*

192 The influence of DS concentrations on the absorbance at 222.5 nm is shown in Fig.  
193 1 and Table 1. The results indicated a strong correlation between the 222.5 nm  
194 absorbance and the DS concentration. The absorbance at 222.5 nm increased in

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

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

204

### 205 *3.2. Influence of dissolved solids and DBS on the absorbance at 400 nm*

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

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

213

### 214 *3.3. Relationship between absorbances of the two spectra*

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

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

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

232

### 233 *3.4. Elimination of the influence of the dissolved solids on the measurement of DBS* 234 *concentration*

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

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

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

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

$$250 \quad y(\text{DOM})=Ax(\text{DOM})+B \quad (1)$$

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

$$255 \quad C=ay(\text{DBS})+b \quad (2)$$

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

$$261 \quad y(\text{DBS}+\text{DOM}) = y(\text{DBS}) +y(\text{DOM}). \quad (3)$$

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

$$264 \quad x(\text{DBS}+\text{DOM})= x(\text{DOM}) \quad (4)$$

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

$$267 \quad C=a[y(\text{DBS}+\text{DOM})-\{Ax(\text{DBS}+\text{DOM})+B\}]+b \quad (5)$$

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

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

$$276 \quad C = ay(\text{DBS} + \text{DOM}) + b. \quad (6)$$

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

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

287

### 288 *3.5. Influence of the sodium chloride concentration of the dissolved organic matter-* 289 *extracted solution on the absorbances*

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

293 regression lines between the DS concentration and absorbances at 222.5 nm and 400  
294 nm spectra for 0.1 mmol NaCl/L and 10 mmol NaCl/L conditions are given in **Table 1**.  
295 The coefficients of determination ( $R^2$ ) between DS concentration and absorbance at  
296 222.5 nm and 400 nm for the 0.1 mmol NaCl/L solution were higher than for 10 mmol  
297 NaCl/L solution (Figs. 1 and 2). A similar trend was observed for correlations between  
298 the absorbances at 222.5 nm and 400 nm spectra.

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

305

#### 306 **4. Discussion**

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

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

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

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

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

339 Stronger positive correlations between the DS concentration and the absorbances at  
340 222.5 nm and 400 nm were observed in the present study under lower concentrations  
341 of the electrolyte solution (**Fig. 1; Table 1**). It was assumed that the lower DS  
342 concentrations at higher NaCl concentrations resulted in a weaker correlation (**Table**

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

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

366 As shown in Fig. 5 (b), for the 10 mmol NaCl/L solution, the deviation of the  
367 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

375 **5. Conclusions**

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

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

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397

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404

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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	<b>0.992–0.995</b>	0.398–0.917	0.021–0.022	0.0029–0.0033
DS conc. vs. Abs. at 400 nm	<b>0.986–0.989</b>	0.807–0.896	0.0036–0.0037	0.00036–0.00037
Abs. at 222.5 nm vs. Abs. at 400 nm	<b>0.989–0.997</b>	<b>0.661–0.949</b>	5.9	7.8–9.8

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## FIGURE CAPTIONS

567

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

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

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

577 **Figure 4:** Linear regression relationships established from the absorbance values at  
578 222.5 nm and 400 nm to eliminate the influence of dissolved solids (DS) in the  
579 dodecylbenzenesulfonate (DBS)–DOM complex solutions.

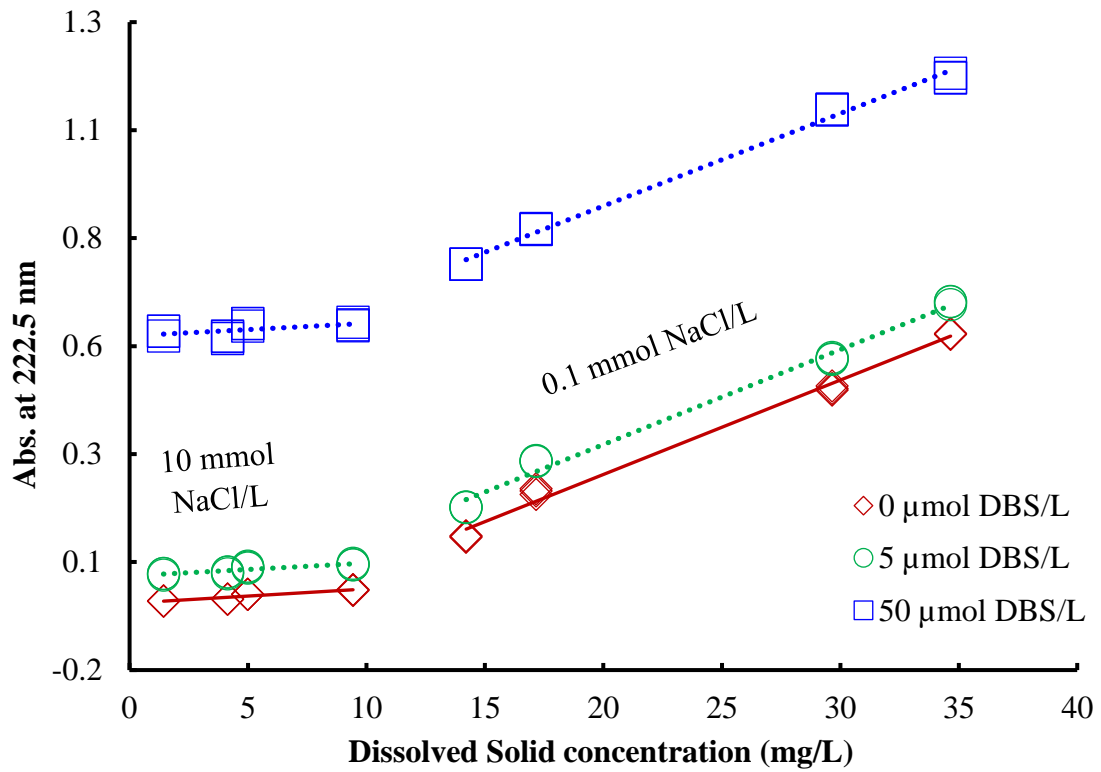
580 **Figure 5:** Relationship between the actual and measured dodecylbenzenesulfonate  
581 (DBS) concentrations for DBS–DOM complex solutions with (a) 0.1 mmol NaCl/L and  
582 (b) 10 mmol NaCl/L before the elimination of the influence of dissolved solids (DS).  
583 The dotted line is the standard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

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

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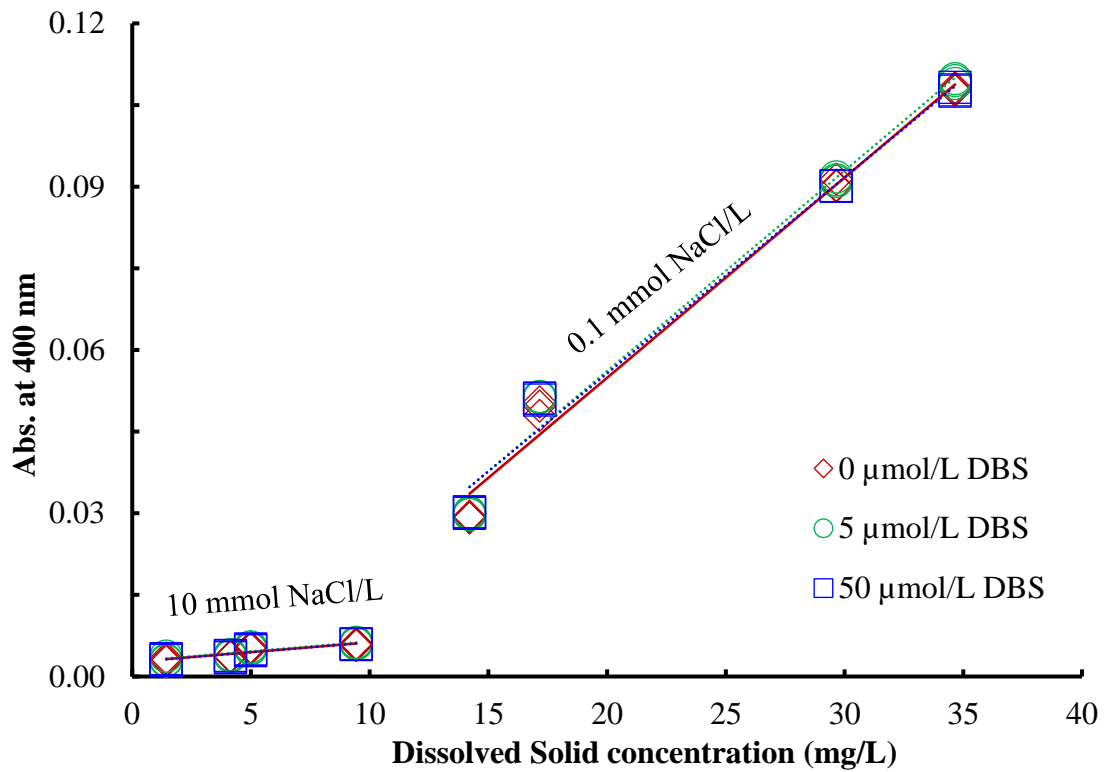
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**Figure 1:** Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations on the 222.5 nm spectrum for the 0.1 mmol NaCl/L and 10 mmol NaCl/L conditions.

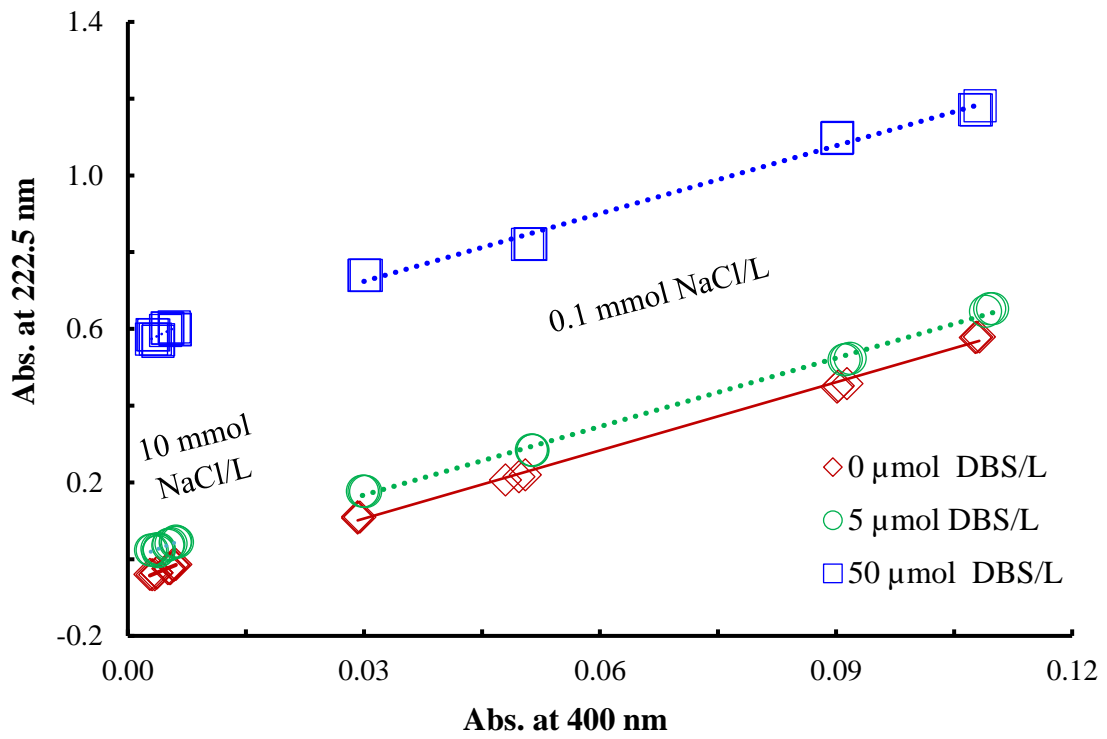
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**Figure 2:** Effects of dissolved solids (DS) and dodecylbenzenesulfonate (DBS) concentrations on the 400 nm spectrum for the 0.1 mmol NaCl/L and 10 mmol NaCl/L conditions.

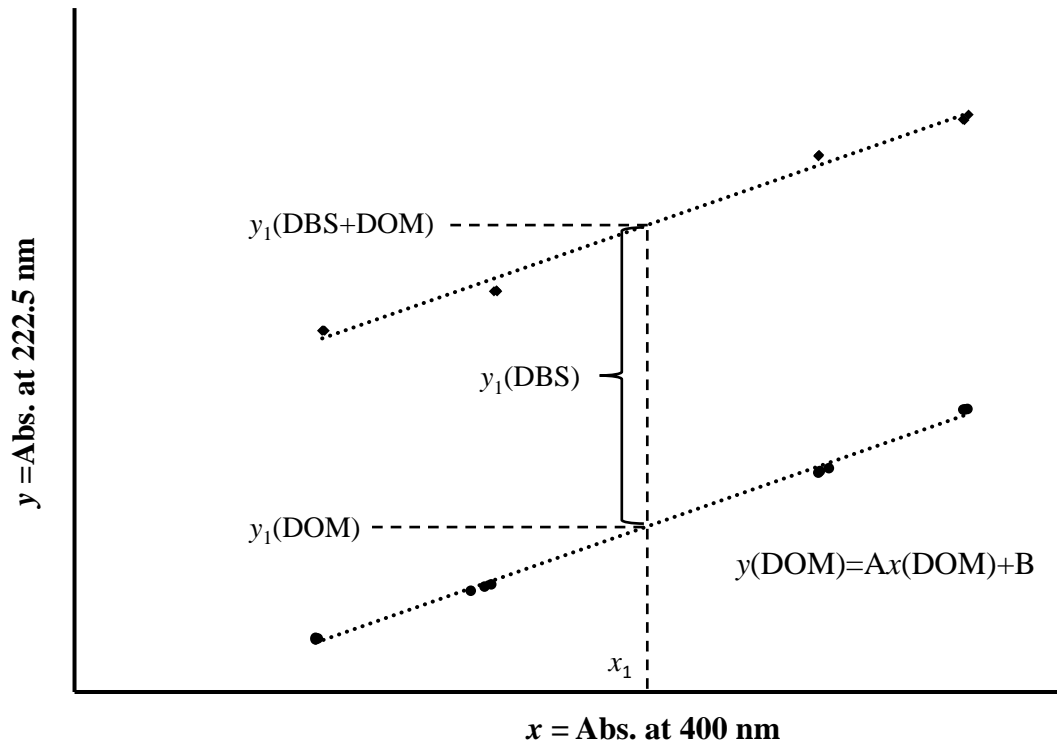
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**Figure 3:** Relationships between the absorbance at 222.5 nm and 400 nm UV-vis spectra measured with respect to the dodecylbenzenesulfonate (DBS) concentration in the 0.1 mmol NaCl/L and 10 mmol NaCl/L solutions.

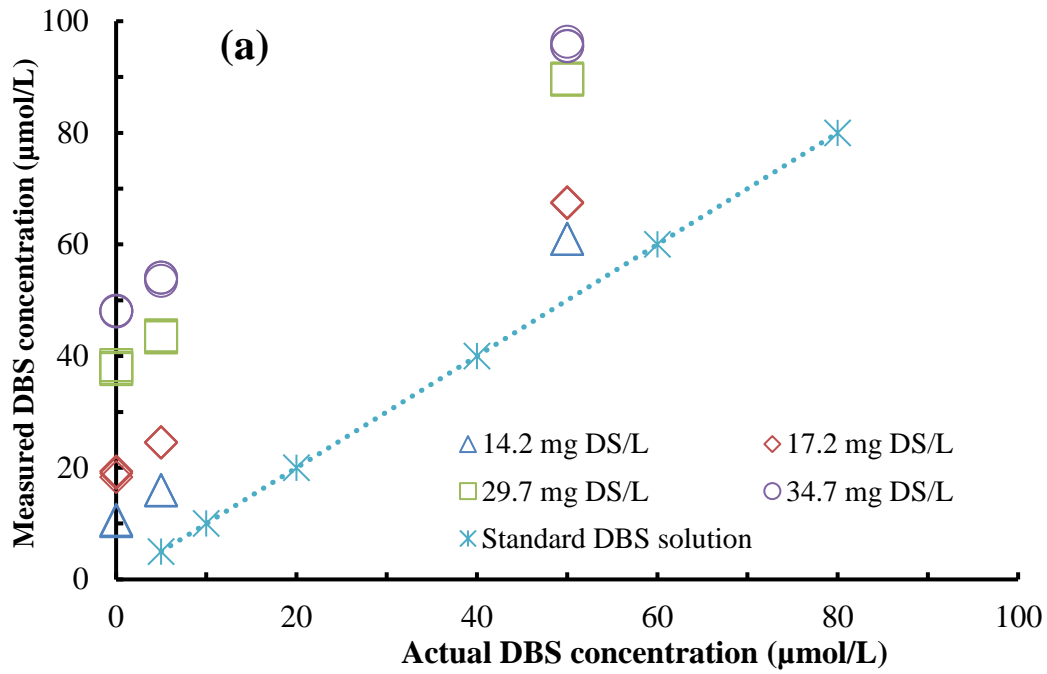
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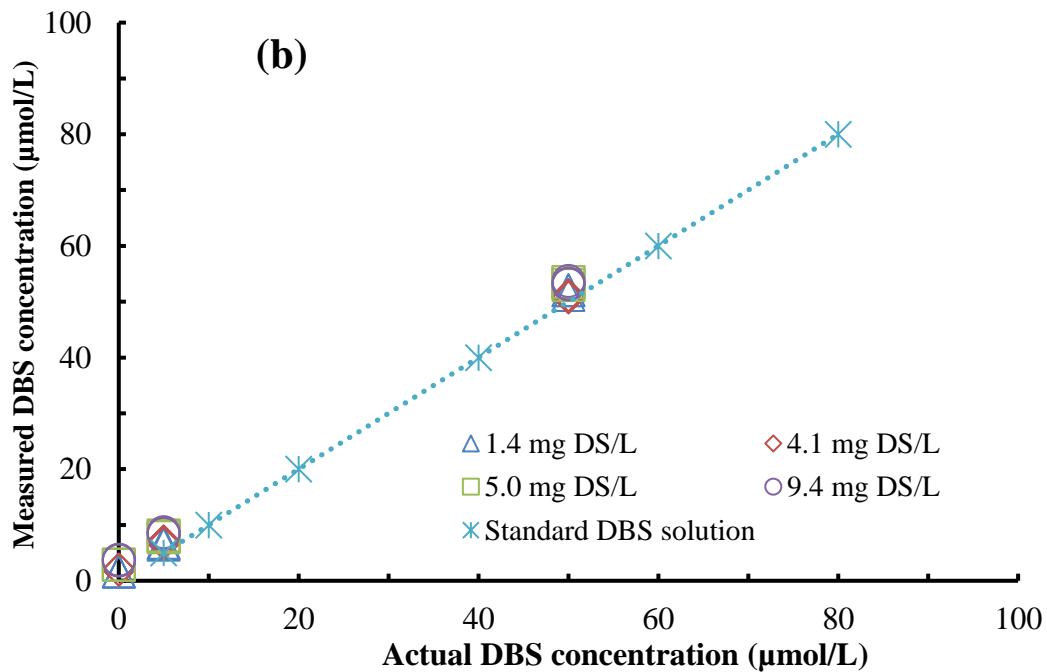
**Figure 4:** Linear regression relationships established from the absorbance values at 222.5 nm and 400 nm to eliminate the influence of dissolved solids (DS) in the dodecylbenzenesulfonate (DBS)–DOM complex solutions.





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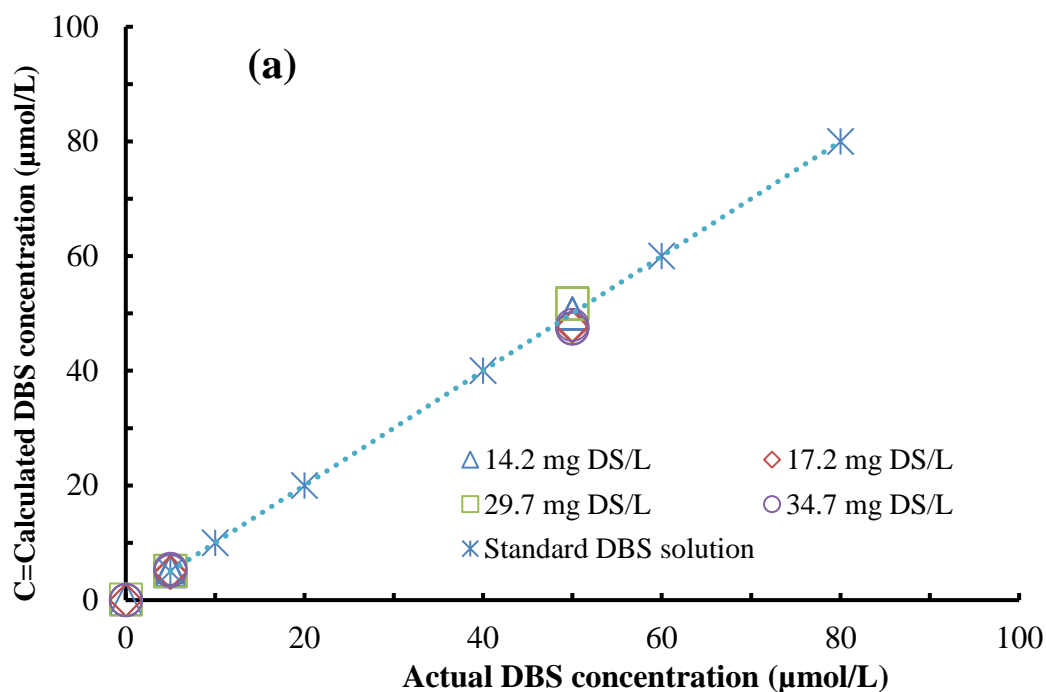
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632 **Figure 5:** Relationship between the actual and measured dodecylbenzenesulfonate

633 (DBS) concentrations for DBS–DOM complex solutions with (a) 0.1 mmol NaCl/L and

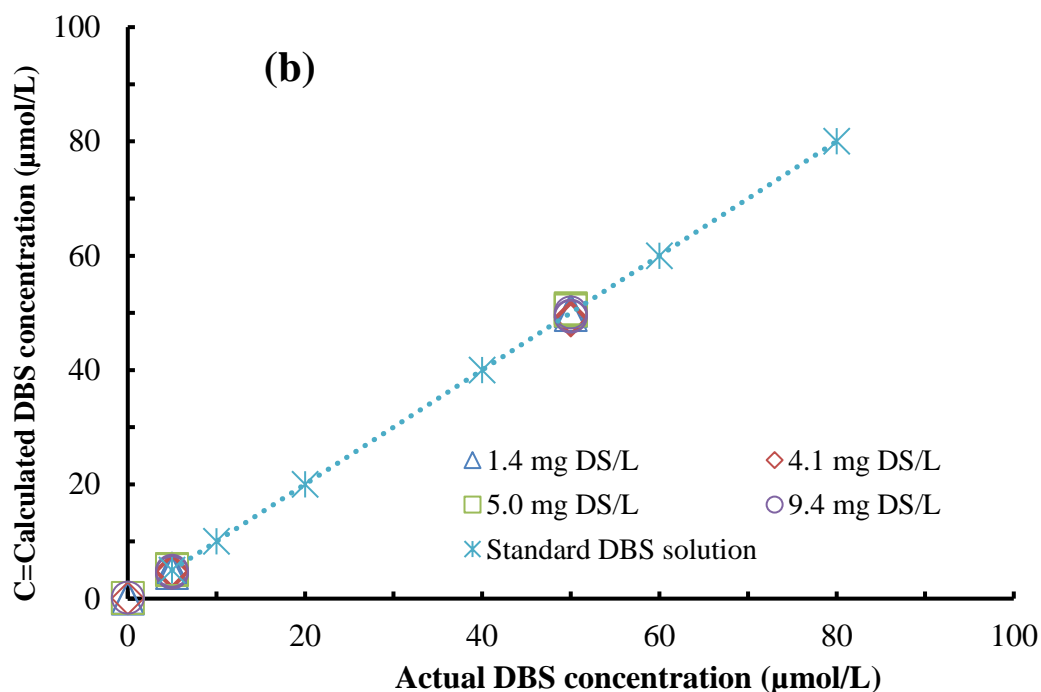
634 (b) 10 mmol NaCl/L before the elimination of the influence of dissolved solids (DS).

635 The dotted line is the standard DBS curve.



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

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