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Simple determination of nonionic surfactants inh ighly-polluted aqueous samples

Research Article

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Abstract: This study examined the direct spectrometric method for determining non-ionic surfactants in highly-polluted samples (*i.e.*, soil leachates) containing high concentrations of humic acids. Meso-tetra-(3,5-dibromo-4-hydrooxyphenyl)-porphyrin served as a coloration agent. The method was tested by use of two polyethoxylate/polypropoxylate – based non-ionic surfactants: Triton CF-21 containing aromatic groups in the structure and Novanik 1047A containing only linear hydrocarbon chains. The main goal was to quantify the influence of interfering species to the results. A test for coincidence of regression lines was employed for objective evaluation of the humic acid influence on the determination. It was observed that for linear surfactant Novanik 1047 A the method provides reliable result and thus, can serve for routine analyses. Regarding Triton CF-21, an interfering effect of humic acids was observed; however, after sufficient dilution of the samples, the method can be used as well. Finally, the method can be used for simple analyses of problematic samples without complicated sample-pretreatment.

Keywords: *Nonionic surfactant • Soil leachate • Spectrophotometric determination • Pb(II)-T(DBHP)P*

1. Introduction

Nonionic surfactants, typically including alkylphenol ethoxylates or aliphatic alcohol ethoxylates, are produced and consumed in large amounts as components of industrial and domestic detergents [1]. Non-ionic surfactants can also dissolve non-polar organic substances in aqueous solution, which provides the possibility of leaching of the non-polar pollutants from soils, sediments, sludge or other similar solid hazardous materials [2,3]. The soil remediation technology based on leaching with surfactant solution is most frequently considered in connection with the remediation of environmental pollutions by persistent organic pollutants (POPs) [4,5]. And so the goal of many scientific studies in recent years has been the research of surfactants application in remediation technologies [6-9].

A specific question which all researchers of surfactants application in soils remediation have to address is a suitable analytical method for the surfactant determination in the soil leachates. These specific environmental samples contain a higher level of interfering substances (mainly humic acids) than other environmental samples, such as wastewaters. Many methods for non-ionic surfactants determination have been developed [10]. These methods have been developed for analysis of either pure surfactants, or aqueous solutions with relatively few interfering compounds. From wide spectra of the methods described in literature, only chromatography provides relevant results without influence of interferences during analysis of environmental samples [11]. Unfortunately, the chromatography is a time-consuming method, requiring expensive instrumental equipment; thus chromatography is not an optimal method for routine analysis of many samples for small laboratories.

To solve the problem with interferences of environmental samples when non-chromatographic methods are considered (for example spectrophotometry), various laboratory processes for the sample purification/surfactant separation have been suggested, but all of them are also extremely time-consuming and, in addition, provide limited positive impact to the results quality

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[10]. This experience was confirmed by our previous experiments as well. The optimal method for routine analysis of wide series of samples should be simple and fast, without the necessity of sample purification.

In 2003, a study describing a new promising spectrophotometric analytical method for polyethoxylated non-ionic surfactants was published [11]. This method uses a coloration complex Pb(II)-T(DBHP)P from meso-tetra-(3,5-dibromo-4-hydrooxyphenyl)-porphyrin (T(DBHP)P) for the determination of non-ionic surfactant Triton X-100 containing aromatic group in its molecule; the authors refer to possible interfering influences. Experimental results proved that the influence of the interferences was low. Unfortunately, the study is focused on the application of the new method for the analysis of wastewater only. Considering that interfering substances concentration in the soil leachates is usually substantially higher than in wastewater, the method cannot be applied to the soil leachates analysis without further detailed study.

This study examines whether the method could be suitable for analysis of the soil leachates, where humic acids could be considered as the main possible interfering substances. We would like to present the following issues: check basic experimental procedures, quantify an influence of the humic acids on analysis results and check the possibility of the application method to determine non-ionic surfactants containing no aromatic groups. We used also a linear surfactant as an example of environment-friendly surfactant, because negative environmental impact of alkyl-phenols is known [12]. This is why the aromatic type of surfactants (alkyl-phenol based) is not a preference in soil remediation.

2. Experimental procedure

2.1. Apparatus and reagents

The absorption spectra were recorded and measured on the Jasco W-530 UV-VIS spectrophotometer using a 1-cm glass cell. T(DBHP)P was synthesized in the Department of Organic Chemistry (Institute of Chemical Technology in Prague, Czech Republic) by the method according to the published study [11,13]. The T(DBHP)P solution was prepared by dissolving 0.02 g of T(DBHP)P in 50 mL of N,N-dimethylformamide (DMF). The lead solution required to prepare the coloration complex Pb(II)-T(DBHP)P was prepared by diluting the stock lead nitrate solution (with lead concentration of 5.00 g L^{-1}): 3 mL of the solution was added into the 100 mL volumetric flask which was then filled up to the mark by the distilled water. The Pb(II)-T(DBHP)P coloration complex was then prepared exactly the same way as delineated in the published study [11]. The solution was refrigerated at 3°C.

Two non-ionic surfactants were used for the evaluation of the method: Triton CF-21 supplied by Sigma-Aldrich and Novanik 1047 A supplied by Sloveca Bratislava (Slovakia). Triton is formed by octylfenylpolyethoxlate while the structure of Novanik does not contain an aromatic group – it is linear alkyl (C12) polyethoxylate(10) polypropoxylate(6). The desired solutions of both surfactants were prepared in distilled water. We used the humic acid sodium salt supplied by Sigma-Aldrich. as a source of humic substances .

2.2. Experimental

The experimental methodology of the analysis used in this study was (if not explicitly described differently) as follows: adding a suitable volume of both the surfactant solution and the coloration complex into the volumetric flask (25 mL) and filling up the volume by the distilled water. The absorbance of the final colored solution was measured. We express the solution concentration as the concentration of the surfactant (mg L^{-1}) in a 25-mL flask after it has filled to the mark, if it does not pointed out differently.

The authors recommend as part of their study [11] the measuring of the absorbance immediately after the sample colorization, but we decided to check the time-progress of the absorbance.

For this purpose we used 0.5 mL of the Triton CF-21 solution (5.46 g L^{-1}) with a 2 mL of coloration complex. The absorption spectrum was measured between 400 and 550 nm after a designated time (1-cm cuvette). The second basic experimental condition examine was the volume of colorization complex added into the sample in 25-mL volumetric flask. Authors [11] recommend using 2.5 mL. With respect to the practical side of laboratory practice, we wanted to test if ,for example, 2 mL of the coloration complex could provide similar results, as the use of the 2-mL non-divided pipette should be more precise than the 2.5 mL divided pipette or another possible equipment for dosing 2.5 mL of the coloration complex. We measured the absorbance (wavelength of 479 nm) of the samples of Triton (dose 0.5 mL, 5.46 g L^{-1}) colorized by the addition of various volumes of the coloration complex (from 1 to 4 mL).

As the last step of the preliminary experiments, we measured calibration curves for both surfactants by using 2 mL of the colorization complex 5 minutes after colorization. Measuring was carried out on a fixed wavelength of 479 nm in Novanik while we

recorded spectra between 500 – 550 nm for the Triton to demonstrate the spectral changes in dependence on the surfactant concentration.

Experiments that focused on the evaluation of analytical results achieved in samples that contained humic acids were based on evaluation of a number of calibration curves measured in the presence of various concentrations of the humic acid. If the non-ionic surfactant determination using T(DBHP)P should provide correct results, the following equation must be valid (under fixed wavelength):

$$A_{(HA+NIS+CA)} = A_{(HA)} + A_{(NIS+CA)}. \quad (1)$$

The $A_{(HA+NIS+CA)}$ in Eq. 1 means absorbance of the sample containing both the non-ionic surfactant and humic acids after its colorization, $A_{(HA)}$ means absorbance of non-colorized sample containing both the non-ionic surfactant and humic acids (where absorbance is caused only by humic acids native color) and $A_{(NIS+CA)}$ means absorbance of the colorized sample, but without influence of the humic acids (we cannot measure this value directly, absorbance is given only for colorized non-ionic surfactant). If Eq. 1 were valid, there would be no additional absorbance caused by the interaction of the colorization agent with the humic acids in the sample. Finally, it will be possible to calculate the value of $A_{(NIS+CA)}$ and evaluate the desired non-ionic surfactant concentration through a simple calibration curve measured for pure surfactant.

The experimental verification of the Eq. 1 was carried out. Firstly, the absorbance (479 nm) of pure humic acid solutions with concentrations of 2.68, 5.36, 8.04, 10.7, 13.4 and 26.8 mg L^{-1} were measured. Thus, we obtained the $A_{(HA)}$ values from the Eq. 1. Secondly, we measured the calibration curves of Triton CF-21 in presence of the humic acid with the above mentioned concentrations (479 nm, 5 minutes after colorization).

The concentrations of humic acids in the calibration samples refer to the final concentrations after filling up the 25-mL volumetric flask by distilled water. We obtained the $A_{(HA+NIS+CA)}$ values in Eq. 1 in this way and then, the desired values $A_{(NIS+CA)}$ were calculated. Finally, we obtained the calibration curve in the pure aqueous solution (as described above) and six calibration curves differing in concentration of humic acid in the solutions. Subsequently, we measured the same data for Novanik for concentrations of humic acid 2.68, 8.04, 13.4 and 26.8 mg L^{-1}. We reduced the number of humic acid concentrations based on experience with results achieved for Triton (no significant differences were observed), but we covered the same range.

2.3. Data evaluation

The objective of the data evaluation was to check a statistical agreement between calibration curve obtained for pure systems and curves obtained in presence of the humic acid. Thus, we compared six twins of the calibration curves for Triton and four twins for Novanik. If it were proven that the curves were statistically identical, the existence of a no interfering effect of humic acid on the determination would be proven as well (in the concentration range of humic acid tested). For this statistical evaluation, the test for coincidence of regression lines was used [14]. The test consists of two steps: the test of variances coincidence and the main test for coincidence of regression lines. The theory of the test is described in a cited literature source [14].

3. Results and discussion

3.1. Examination of basic experimental conditions

The preliminary experiments were carried out to check the basic experimental parameters of the analysis before the subsequent examinationof humic acid d the results. Fig. 1 shows the absorption spectra of the colored solution of Triton CF-21 at three holding times. The Fig. 1 scale is focused on the most important absorption band (479 nm). In contrast to the previous study [11], it is obvious that 2 minutes of coloration is insufficient to achieve a stable absorbance (at 479 nm). Nevertheless, the difference between absorbance after 5 and 20 minutes was insignificant (less than 0.01). Thus, we decided to keep the 5 minute coloration time in all subsequent measurements.

Fig. 2 shows the influence of the coloration agent volume on absorbance. The figure indicates that, in agreement with the previous study [11], absorbance does not further increase after the addition of 2.5 mL

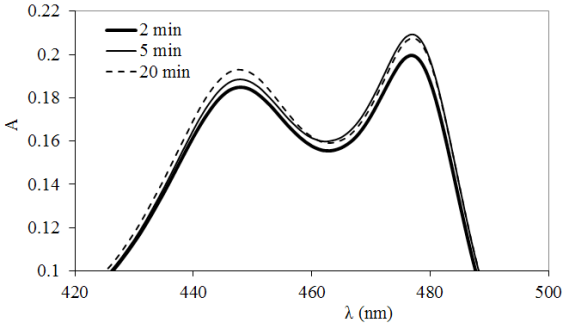

Figure 1. Absorption spectra of Pb(II)-T(DBHP)P-Triton CF-21 complex (0.11 g L^{-1}) after various time from the coloration agent addition (axis scale is chosen to emphasize the wavelength of interest- second band).

of the coloration agent. However, the difference between the absorbance achieved by 2 mL and 2.5 seems to be insignificant. Thus, we decided to choose the addition of 2 mL of the coloration agent.

Fig. 3 shows the calibration curve for Triton CF-21. The dependence has a sigmoidal shape. Linearity can be found between concentrations 40 and 160 mg L^{-1} with a square variance of 0.9954. No increase of absorbance between 0 and approx. 40 mg L^{-1} was observed. This is the reason why the calibration cannot be used for lower concentrations. This behavior is recognizable also in Fig. 4, where there is no difference between absorbance for blank solution and for 22 mg L^{-1} (at 479 nm). By extrapolation of the regression line (Fig. 3), we can estimate the determination limit of about 30 mg L^{-1}. It does not correspond with the published study [11], where the limit of detection 0.02 mg L^{-1} was deduced.

Also the linearity range does not correspond with the previous study, where the range of 0 – 800 mg L^{-1} was mentioned, although surfactant TritonX-100 used in the cited study is similar to our Triton CF-21. However, our results probably correspond with the critical micelle concentration (CMC) of Triton CF-21 (about 130 mg L^{-1}) [15]. The results indicate that linearity is found approximately under the CMC, while above this concentration, the increase of absorbance is very low. It may correspond with more-less constant surfactant monomer concentration when the overall concentration increases above the CMC [16]. It can be explained that the surfactant molecules bound in the micelles cannot react with the coloration agent. Furthermore, several methods for the CMC determination are based on absorbance measuring with a suitable coloration agent [17]. Finally, our observation corresponds with general surfactants behavior. We cannot explain why the linearity was measured so wide in the cited study, because the Triton X-100 CMC is about 140 mg L^{-1} [18].

Fig. 5 shows the calibration curve for Novanik 1047A. Spectral changes were almost identical with those of Triton. Linearity of the calibration dependence was proven between concentrations 11 and 50 mg L^{-1}, while the determination limit can be estimated about 10 mg L^{-1}. Since the CMC of Novanik 1047 A is about 50 mg L^{-1} [15], the beginning of non-linear calibration corresponds with the CMC effect, as it was mentioned above. Comparing the slopes of linear interpolations of the calibration curves, the method sensitivity for Novanik 1047 A (5.99) is substantially higher than for the Triton CF-21 (1.98). It reflects the number of polyethoxylate and polypropoxylate groups in the

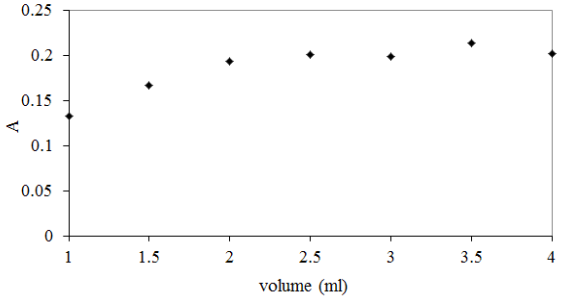

Figure 2. Influence of volume of the coloration agent on absorbance of Triton CF-21 solution (0.11 g L^{-1}).

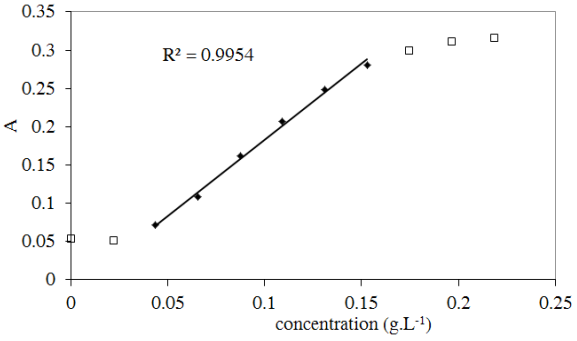

Figure 3. Calibration curve for Triton CF-21 (no humic substances).

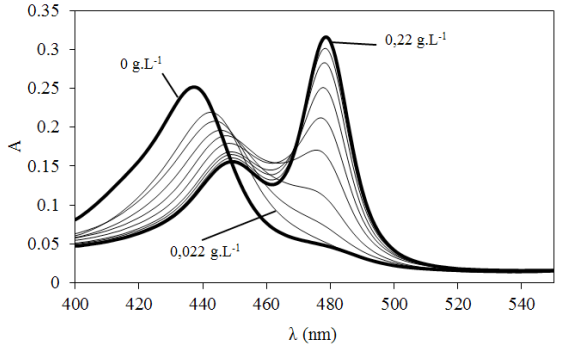

Figure 4. Spectral changes during the measurement of the calibration curve of Triton CF-21; thin curves are spectra for increasing concentrations (absorbance are marked at fixed wavelength in the Fig. 3); curve for 0 g L^{-1} represents absorption spectra of Pb(II)-T(DBHP)P coloration complex without any surfactant.

Table 1. Absorbance of humic acid solutions.

humic acid sodium salt concentration (mg L^{-1})	2.68	5.36	8.04	10.7	13.4	26.8
absorbance (479 nm)	0.0103	0.0202	0.0300	0.0400	0.0499	0.0981

surfactant molecules [11]. It seems that the non-polar part of the molecule has no negative effect on the method sensitivity (Novanik contains no aromatic groups). This is a highly positive observation, because linear surfactants are preferred from the environmental point of view, thus, analysis of such samples are expected to be more desired.

3.2. Humic acids influence on the determination

The first step, measured the absorbance of humic acid solution without a surfactant or coloration agent. The results are summarized in Table 1, and these values represent the $A_{(HA)}$ parameter in the Eq. 1.

Calibration curves for Triton CF-21 for various concentrations of humic acid are displayed in Fig. 6. Only four curves were displayed to keep the figure lucid. It is obvious that curves look identical, differing only in constant additional absorbance caused by the humic acid (see Table 1). Curves for the rest of the humic acid concentrations were of the same shape and appropriate positions (according to the humic acid concentration).

The remaining test for coincidence of regression lines would objectively decide if the curves were identical with the only difference in the additional constant absorbance. First, humic acid absorbance was subtracted from each point in the particular curve (Table 1). Then, the curve was compared with the curve measured in the system containing no humic acid. All twins of the calibration curves for all humic acid concentrations are displayed in Fig. 7 for Triton CF-21 and in Fig. 8 for Novanik 1047A.

The first step of the statistical evaluation consisted in test of variances coincidence for each couple of the lines. It was found that all twins of the lines have identical variances. Thus, the test for the coincidence of regression lines was carried out.

For all couples of the lines, the test statistics F_A was calculated and these numbers were compared with the tabulated quantile values defined for the particular number of points and curves under desired significance level α (usually chosen 0.01, 0.05). The tabulated quantiles values ($F_{1-\alpha}$) for the comparison with the test statistics F_A were $F_{0.99}$ = 10.9 and $F_{0.95}$ = 5.14 for Triton and $F_{0.95}$ = 6.94 and $F_{0.90}$ = 4.33 for Novanik. Due to the results, weaker values of significance levels for Novanik were selected. Calculated F_A values for both surfactants are listed in Table 2. If the particular F_A value is higher than the quantile, it can be interpreted that the lines are different with probability of 1-α.

So, for Triton, one couple of the lines is deferent with a high probability of 99% (F_A=13.2) and two other twins (F_A=5.91 and 5.21) with probability of 95%. The rest of the twins cannot be marked as different with significant probability. What is interesting is that there was no trend observed between the humic acid concentrations and F_A. The difference between the calibration lines (w/o humic acid) does not increase with the humic acid concentration in the sample. Nevertheless, results showed that it is suitable to dilute the samples which have a relatively higher absorbance caused by humic acids before the coloration. However, it could not cause any practical problems since a higher concentration of humic acids (which are normally almost insoluble) in the

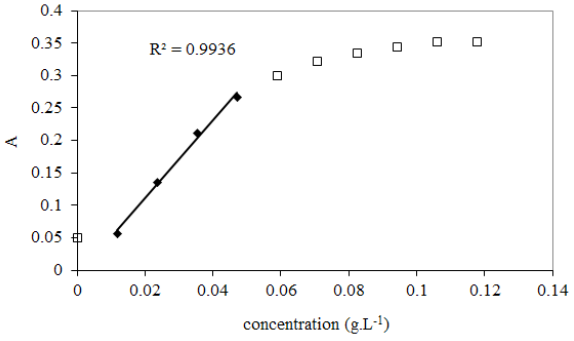

Figure 5. Calibration curve for Novanik 1047 A (no humic substances).

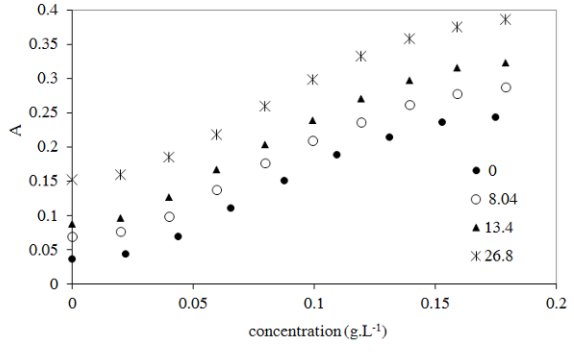

Figure 6. Calibration curves for Triton CF-21 for various concentrations of humic acid (mg L^{-1}).

Table 2. Test statistics F_A for all twins of the regression lines of both surfactants (each number is for curve in pure system compared with one curve measured in the presence of humic acid); see Figs. 7 and 8.

humic acid sodium salt concentration (mg L^{-1})	2.68	5.36	8.04	10.7	13.4	26.8
F_A - Triton CF-21	3.82	4.34	5.91 (>$F_{0.95}$)	1.35	5.21 (>$F_{0.95}$)	13.2 (>$F_{0.99}$)
F_A - Novanik 1047 A	0.13	-	0.71	-	0.51	0.31

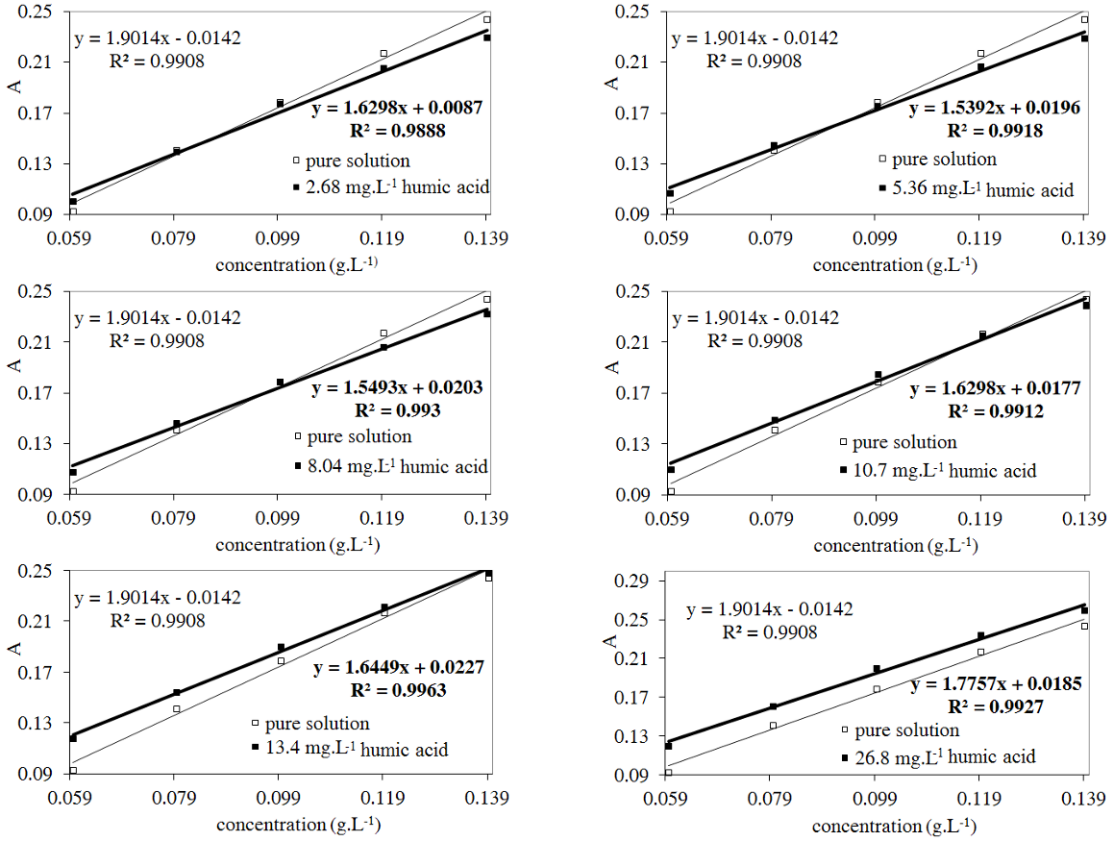

Figure 7. Calibration curves for Triton CF-21: comparison of curve measured in presence of particular humic acid concentration (where absorbances were lowered about absorbance of humic acid solution with the same concentration, see Table 1) with the calibration curve achieved in the system containing no humic acid.

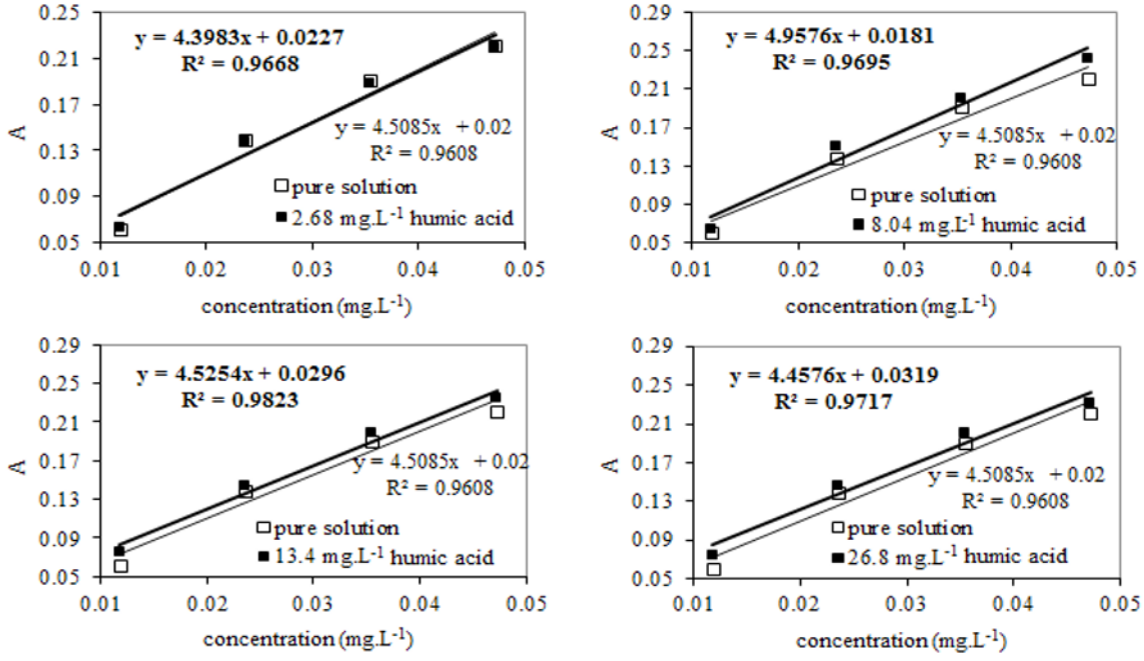

Figure 8. Calibration curves for Novanik 1047A: comparison of curve measured in presence of particular humic acid concentration (where absorbances were lowered about absorbance of humic acid solution with the same concentration, see Table 1) with the calibration curve achieved in the system containing no humic acid.

samples are usually conditioned by a high concentration of the surfactant. Diluted samples, thus, should have both – less own absorbance caused by humic acid and less concentration of the surfactant overlying closer to the calibration range.

For Novanik, all F_A values were substantially lower even than quantile $F_{0.9}$.Thus, all couples of the lines cannot be marked as different, even using a significance level of 90%. Finally, influence of the humic acid on the determination of non-ionic surfactant Novanik 1047 A was not observed.

4. Conclusions

Direct spectrometric determination of two non-ionic surfactants in the presence of humic acid using previously published coloration agent was examined. Related to the basic experimental conditions, we observed that 2 mL of coloration agent is sufficient for coloration of the sample; 5 minutes is the desired time for the achievement of stable absorbance. For Triton CF-21, the linearity of calibration in range of 40 – 160 mg L^{-1} and the determination limit of about 30 mg L^{-1} was observed. Such behavior probably corresponds with the CMC value. Related to the Novanik 1047 A, the linearity in range of 11- 50 mg L^{-1} and the determination limit of about 10 mg L^{-1} was observed. Sensitivity of the method is substantially higher for Novanik, what is given by a higher number of poyethoxylate and propoxylate groups in the surfactant molecule.

Regarding Triton in some cases, the influence of the presence of humic acid in the sample on the determination was proven. However, the samples were diluted anyway in most cases so that the influence of the impurities were expected to be minor. No interfering effect of humic acid was observed in Novanik. This observation is highly positive since non-aromatic surfactants are preferred in environmental applications. The method looks to be suitable for routine simple analyses of non-ionic surfactants in the samples containing humic species (for example soil leachates). In addition, further tests with several real soil leachates also proved the usability of the method. However, this method cannot be recommended in general for all sample types and compositions. If reliable results are desired real soil leachates, it would be necessary to carry out similar tests as described above to exclude interferences with other impurities. Furthermore, the CMC value of surfactants can be influenced by overall composition of the solution (it can, theoretically, influence the calibration range). Nevertheless, we can recommend the method for the simple determination and routine analyses, for example in environmental research laboratories; this is the purpose for method development.

The following recommendations for the simple application of the analytical method can be provided as follows:

1. measuring of the solution absorbance (479 nm, 1-cm cuvette) prepared by the transfer the of known volume of the sample into a 25-mL volumetric flask filled up to the mark by distilled water; If the absorbance overlaps approximately by 0.05, the sample should be more diluted (by use of less sample volume dosed into the 25-mL flask). The measured value represents A(HA) in the Eq. 1;
2. transfer of equal volume of the sample as in the point 1 into 25-mL volumetric flask, dose of 2 mL of coloration agent and filling up to the mark by distilled water, measuring of absorbance (479 nm) after 5 minutes; Measured value represents A(HA+NIS+CA) in the Eq. 1;
3. calculation of A(NIS+CA) from the Eq. 1;
4. evaluation of non-ionic surfactant concentration from the calibration line measured in water containing no humic acid. If the absorbance is out of the calibration range, the sample must be more diluted (start from the point 1).

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