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SOLVENT EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF ANIONIC SURFACTANTS IN WASTE WATER WITH CATIONIC DYES

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ABSTRACT. Anionic surfactants have large applications in household cleaning and in many industrial fields but they are also environmental pollutants. We used the solvent extraction-spectrophotometric method to determinate the anionic surfactants in aqueous solutions and waste water samples using cationic dyes. We determined the effects of experimental variables as pH, dye concentration, shaking and standing time and we discovered the best procedure. We followed the pollution level of Săsar River during the first six month in 1996-1998. We tested the concordance between the extractive-spectrophotometric method with ethyl violet and the standard methylene blue method.

INTRODUCTION

Surfactants are playing an increasingly important role in industrial applications and household cleaning. Typical anionic surfactants contain anionic and hydrophobic part and both contribute to the surfactant physicochemical properties. The most important classes of anionic surfactants are the long chain alkanesulfonates (RSO_3^-), alkylsulfates ($ROSO_3^-$) and linear alkylbenzensulfonates (LAS). All these anionic surfactants are water-soluble and are widely used in commercial products and processes in which detergent action is required. Anionic surfactants are also environmental pollutants. Although some parts of the anionic surfactants used for washing are discharged into the aquatic environment by sewer systems and waste water treatment plants, considerable parts of them are drained off directly in the aquatic environment. Anionic surfactants have a negative impact on waters because, even in small amount can cause a lowering of the water surface tension. Anionic surfactants emulsify greases and oils, disperse the colloids making difficult their sedimentation. Surfactants produce thin films at the air-water interface and perturb the air-water transport of oxygen with negative effects on the aquatic life.

Due to their large solubility, the surfactants are able to modify the soil permeability and, in certain conditions, to penetrate into and to impurify the underground water.The determination of anionic surfactants at concentration of traces amount is often necessary in waste water control. Among the analytical methods described in the literature, those based on spectrophotometric measurement constitute an important part [1-6].

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Almost all of the methods used for the spectrophotometric determination of anionic surfactants depend on the formation of a salt, an ion associate between the bulky anion of anionic surfactant such as RSO_3^- or RSO_4^- and a cation. The cationic substance can be a basic dye, among them the most known is methylene blue. That's why anionic surfactants are also called methylene blue active substances. The anion of anionic surfactant and the cationic dye makes up a colored and hydrophobic complex, which can be extracted using a suitable organic solvent. The absorbance of this complex, which depends on the surfactant concentration, can be examined with a spectrophotometer.

Other cationic dyes used for anionic surfactants determinations by extractive-spectrophotometric method are methyl green and crystal violet.

We try to use another cationic dye, which forms a hydrophobic ion associate with the surfactant anion according the following reaction:

$$A^- Na^+ \;+\; C^+ X^- \;\rightarrow A^- C^+ \;+\; Na^+ X^-$$

where A^- is the surfactant anion and $C^+ X^-$ is the cationic dye.

To be suitable in the extractive spectrophotometric determination of anionic surfactants, the ionic associate $A^- C^+$ must have a large extractibility into a certain organic solvent and also the organic extract has to present a good molar absorptivity.

Among the cationic dyes we used ethyl violet as reagent in the extractive spectrophotometric method. We used as extracting solvent benzene and toluene. In the paper we followed to establish the best condition for the use of ethyl violet in the anionic surfactants determination in wastewaters, using the solvent-extraction method.

EXPERIMENTAL

During the first six months of 1996 – 1998 we followed the anionic surfactants pollution level for the water of Săsar River that passes through the center of Baia Mare.

We determined the anionic surfactants concentration using the standard method based on methyl blue. For the absorbance measurement we used a spectrophotometer Jenway with glass cells of 10-mm path length and for pH measurements was used a Cast pH meter equipped with a combined electrode. As etalon surfactant for preparing the surfactant solutions with known concentration we used sodium lauryl sulfate from Merck, with the purity of 99%.

We evaluated ethyl violet as a reagent for extractive spetrophotometric determination of the anionic surfactants using sodium lauryl sulfate 3×10^{-7} M and 4×10^{-7} M. It was used a 10^{-3} M solution of ethyl violet. To extract the ionic associate complex between sodium lauryl sulphate and ethyl violet were used benzene and toluene. To mentain the pH sample solution in a certain range we used acetate and phosphate buffer solutions.

After a series of experiments we established the following method: 100 ml from the sample that contains anionic surfactants are introduced into the funnel. Then 5 ml acetate and phosphate buffer, 2 ml ethyl violet solution 10^{-3} M and 5 ml extraction solvent are added. After shaking the funnel for 5 minutes the organic phase is separated from the aqueous phase. The organic phase absorbance is measured at maximum absorbance wavelength (615 nm).

In the case of waste water determination the phases' separation is more difficult. 5 ml sodium sulfate 1 M are added for a faster phases' separation and 90 ml aqueous phase was discarded. This way the phases' separation time was reduced from 20-60 minutes to 1 minute. We tested the concordance between the standard method and ethyl violet method for the anionic surfactant determination. For the measurement were used samples of Săsar River at its emergence from Baia Mare.

RESULTS AND DISCUSSIONS

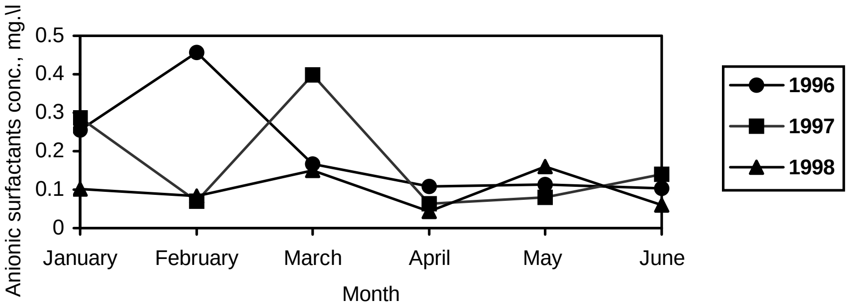

Fig. 1. Levels of anionic surfactant concentrations monitored the first six month, 1996-1998

The anionic surfactant pollution development of Săsar river water during the first 6 months of 1996 - 1998 is represented in figure 1 and 2.

The samples had a concentration of anionic surfactants that varied between 0,1-0,5 mg/l that correspond to a slight anionic surfactant pollution.

A decrease in the level of anionic surfactant pollution of Săsar River was observed.

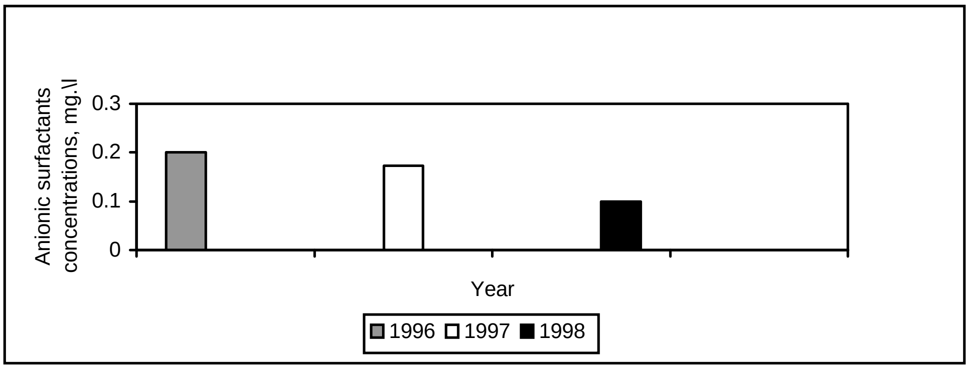

Fig. 2. The average values of the anionic surfactants concentrations at Săsar River, monitored the first 6 month, 1996-1998

This decrease is shown in figure 2 where are presented the average anionic surfactant concentrations for the first 6 months of 1996 - 1998.

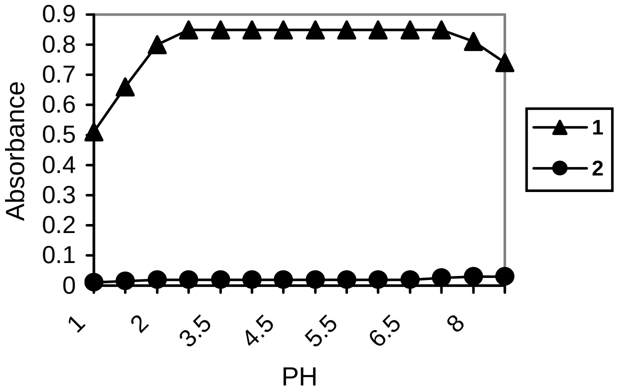

Fig. 3. Effect of pH on the extraction with benzene (anionic surfactant, sodium lauryl sulfate SLS)
Curve 1:benzene extract, [SLS] $_{\text{initially}}$ 4x10^{-7} M, reference, reagent blank)
Curve 2: reagent blank (reference, solvent)

To establish the best working conditions for the measurement of anionic surfactant with ethyl violet we made a series of determinations following the sample pH influence upon the absorbance values. We mentained the ethyl violet volume at 5 ml and the shaking time at 5 minutes. The results are presented in figure 3 and 4.

As it is shown in figure 3 the absorbance of the complex benzene extract was maximum for a pH between 3.5 and 6.5. In this pH range the absorbance is constant. It increases for a pH between 1 and 3.5 and it decreases for pH above 6.5.

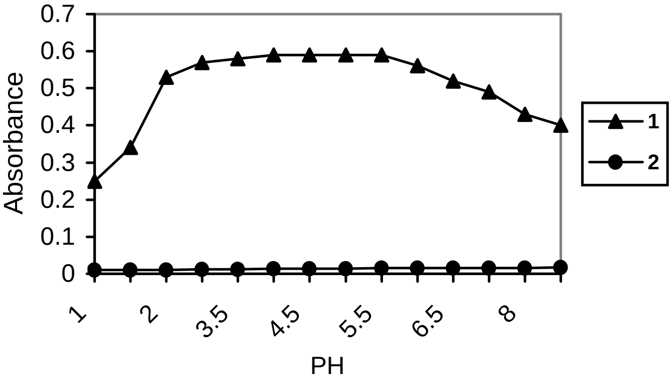

Fig. 4. Effect of pH on the extraction with toluene (anionic surfactant, sodium lauryl sulfate SLS)
Curve 1: toluene extract, [SLS] $_{\text{initially}}$ 3x10^{-7} M, reference, reagent blank;
Curve 2: reagent blank; reference, solvent

In the case of complex toluene extract the absorbance was maximum for a pH between 3.5 and 6,5. Depending on the results obtained we chose pH=5 from the maximum absorbance range.

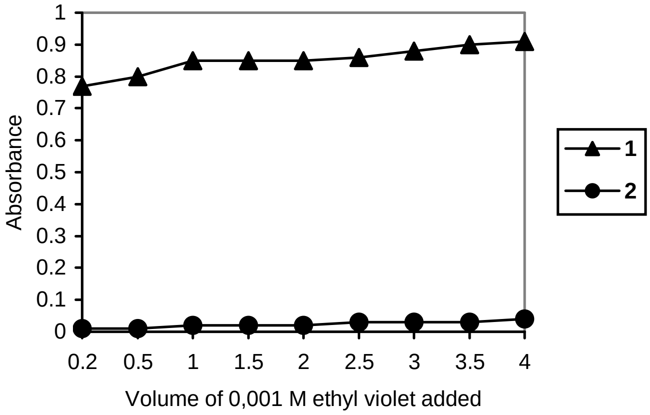

Fig. 5. Effect of 0,001 M ethyl violet volume on the extraction with benzene (anionic surfactant SLS)
Curve 1: benzene extract, $[SLS]_{initially}$=$4x10^{-7}$M; reference, reagent blank)
Curve 2: reagent blank; reference, solvent

In another series of determinations we maintained pH=5 and we varied the ethyl violet solution volume from 0.2 to 4 ml. As it is shown in figure 5 the absorbance was maximum and constant for 1 to 2.5 ml ethyl violet solution for benzene.

In the case of toluene extract maximum and constant absorbances were obtained at the amounts from 1 to 3 ml 10^{-3}Methyl violet. The results are shown in figure 6.

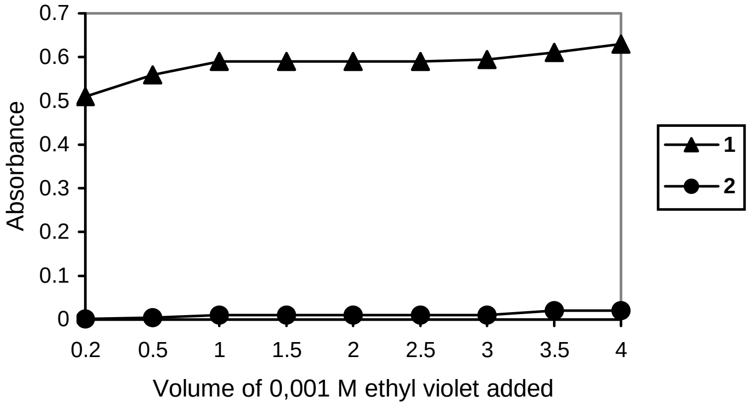

Fig. 6. Effect of 0,001 M ethyl violet volume on the extraction with toluene (anionic surfactant SLS)
Curve 1: toluene extract, $[SLS]_{initially}$=$3x10^{-7}$M; reference, reagent blank)
Curve 2: reagent blank; reference, solvent

Based on the determinations made, we considered pH=5 and 2ml ethyl violet as the best conditions.

It was also examinated the shaking time on the absorbance value. It was found that the value of absorbance is constant for a shaking time above 3 minutes. The experimental determinations were made using a shaking time of 5 minutes.

The wastewater samples contain colloids and suspensions and during the shaking time an emulsion that provides the increase of the time necessar to the separation phases is obtained. But, by adding a 1 M sodium sulfate solution as salting-out agent this time can be reduced from 20 minutes to 1 minute.

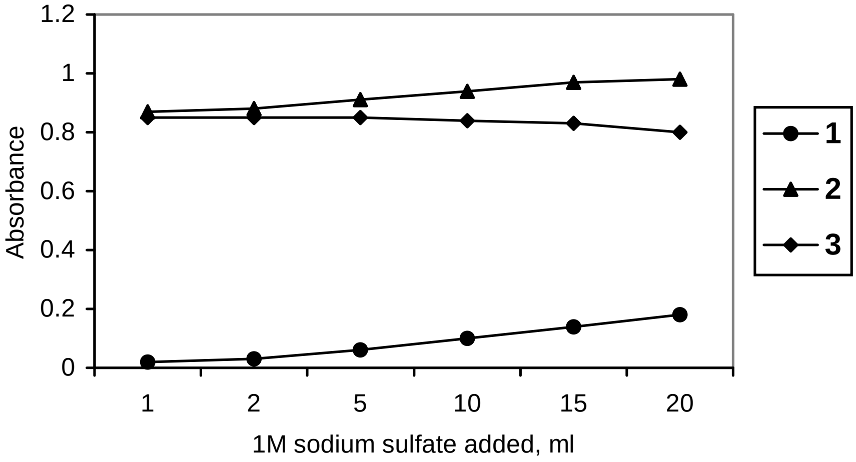

Fig. 7. Effect of salting-out agent (Na_2SO_4 1M) on the extraction with benzene (anionic surfactant SLS)
Curve 1: reagent blank; reference, solvent;
Curve 2: benzene extract, $[SLS]_{initially}=4x10^{-7}M$; reference, reagent blank;
Curve 3: benzene extract, $[SLS]_{initially}=4x10^{-7}M$; reference, reagent blank (net).

It was tested the effect of the salting-out agent volume added to the extraction system. In the case of benzene extraction the reagent blank absorbance increased proportionally with the salting-out agent volume added. The results are shown in figure 7.

The salting-out agent causes the increase of the sample's absorbance and also the reagent blank' absorbance and in conclusion the net absorbance value is not influenced.

In the case of the toluene extraction was observed that the salting-out agent does not influence the absorbance.

The method determined for ethyl violet used for the measurements of the anionic surfactants was tested on 6 samples. Every result is the average of three measurements. The samples from 1 to 3 are from Săsar River and 4 to 6 from the entering into the wastewater treatment plant.

The results obtained are shown in Table 1.They are compared with those from the methylene blue standard method. A good concordance was observed.

Table 1.

Determination of anionic surfactants on wastewater samples

Sample		Concentrates found, mg.\ l	
		Methylene blue method	Ethyl violet method
1.	Săsar River water 1	0,121	0,117
2.	Săsar River water 2	0,044	o,o42
3.	Săsar River water 3	0,016	0,015
4.	Wastewater treatment plant sample 1	0,336	0,319
5.	Wastewater treatment plant sample 2	0,114	0,1o9
6.	Wastewater treatment plant sample 3	0,568	0,557

CONCLUSIONS

The cationic dye ethyl violet was tested as a reagent for the anionic surfactants determination from water. The best procedure was established for pH=5 and 2 ml ethyl violet.

In the case of waste waters to decrease the phases separation time from 20 minutes to 1 minute, 5 ml sodium sulfate solution 1 M was added.

It was found that toluene is more useful than benzene because the reagent blank absorbance is smaller than that of benzene and toluene is less toxic than benzene.

The results of the determinations made with ethyl violet are in good concordance with those obtained with standard method, but ethyl violet method is simpler and faster because a single extraction is necessary.

REFERENCES

1. K. Higuchi, Y. Shimoishi, H. Miyata, K. T∗el, T. Hayami, Analyst, 1980, **105**, 768-
2. D. C. Abbott, Analyst, 1963, **88**, 240-241
3. S. Motomizu, S. Fujiwara, A. Fujiwara, K. T∗el, Anal. Chem., 1982, **54**, 392-397
4. H. Kubota, M. Idei, S. Motomizu, Analyst, 1990, **115**, 1109-1115
5. Y. Shimoishi, N. Saito, H. Miyato, M. Zenki, Analytical Sciences, 1997, **13**, 365-368
6. K. Fytianos, D. Vasilikakis, N. Raikos, J. Environ. Sci. Health, 1997, **A32**, 953-962