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Preliminary Testing for Anionic, Cationic and Non-ionic Surfactants Determination

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Detergents present a major environmental problem due to large quantities of surfactants released from laundries. For this reason, it is important to apply an appropriate analytical method for their determination. In this work, we propose two simple, fast and inexpensive analytical methods for anionic, cationic and non-ionic surfactant determination: thin layer chromatography (TLC) separation for qualitative screening and quantitative potentiometric determination with ion-selective electrodes. These methods have been chosen because of their many advantages: rapidity, ease of operation, low cost of analysis and a wide variety of TLC application possibilities. The advantage of potentiometric titration is its very high degree of automation and very low detection limits obtained with different ion-selective electrodes applied for different surfactants.

Key words: *Surfactants, potentiometric determination, detergents*

Introduction

Different anionic, non-ionic, cationic and amphoteric surfactants (or surface-active species) are used nowadays in different institutions, industries and households in very large amounts. Their industrial application is widespread in the cosmetics, metal-working, mining, paper and leather industries, which is why the surfactants present in detergents represent a major environmental pollutant. They present a serious environmental problem especially in laundries where huge amounts are applied daily: for example, in Western Europe 4 250 000 tons of detergent products and 1 190 000 tons of softener products are used every year.[1] Many commonly used surfactants are highly toxic and dangerous for the environment and human health. This is why the regulations for wastewaters are very strict: in Croatia, the limit for releasing synthetic surfactants into wastewaters is $\gamma = 0.05\text{–}0.1\ \mathrm{mg\ L^{-1}}$.[2] Both the toxicity of surfactants and their biodegradation in the environment are influenced by a variety of interacting physical, chemical and biological factors. The complexity of detergent products with which surfactants are mixed may also lead to a synergistic effect. Furthermore, detergent products can interact with the biodegradation and toxicity of other compounds in the environment.

Chemical analysis of surface-active species is of interest for many applications, such as in process monitoring, biomedical applications, environmental monitoring and surface science investigations.[3] Analysis of surfactants is carried out generally by either chromatographic procedures that need derivatisation like gas or liquid chromatography. Improved analytical procedures for the determination of the entire group of surfactants require optimization of the sample pre-treatment steps. Recent research reports the use of solid-phase micro extraction and solid-phase extraction with different sorbents such as alkyl-bonded silica, graphitized carbon black and styrene-divinylbenzene resins. Sequential solid-phase extraction combined with liquid chromatography mass spectrometry has been successfully employed for the extraction of surfactants.[4]

Thin layer chromatography is a potentially powerful technique for the separation of surfactants. Reversed phase thin layer chromatography can be used to separate entire classes of surfactants (i. e. anionics from non-ionics from cationics). Conversely, silica gel can be used to separate individual anionic or cationic surfactants from other similarly charged surfactants.[5] Thin layer chromatography has advantages because of its numerous positive characteristics: low cost, ease of operation, rapidity, wide choice of adsorbents and solvents, and diversity of techniques and equipment.[6]

Surfactants have the ability to lower surface tension due to their specific structure. All typical surfactant properties can be linked to their structure and to the presence of hydrophilic and hydrophobic groups in the molecule. The hydrophilic group in a surfactant primarily determines its application as well its analytical properties.[7] Since an entire range of instrumental analytical techniques may be used for surfactant analysis, depending on the surfactant class and the problem to be solved, a differentiation must be made as to whether the analysis is to be carried out in the framework for controlling raw materials, quality assurance of manufactured ionic or non-ionic surfactants, monitoring of competitors, quality assurance of formulations, monitoring competitor formulations, environmental samples investigation, investigation of electroplating baths, checking the surfactant content of water-soluble cooling lubricants, or testing anionic surfactants and soaps in washing powders. The standard method of anionic, cationic and non-ionic surfactant determination is UV/VIS determination and the time-consuming standard flask extraction with chloroform,

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in which very large quantities of harmful organic solvent are employed.

This research was a preliminary study on coupling two simple analytical methods (thin layer chromatography with potentiometric titration) for surfactant analysis that can be useful in many applications such as in process monitoring, biomedical applications, environmental monitoring and surface science investigations.[8] Similar advanced methods are being tested recently.[9] Thin layer chromatography was tested since it is a potentially powerful technique for the separation of surfactants. While reversed phase thin layer chromatography can be used to separate entire classes of surfactants, silica gel can be used to separate the individual anionic or cationic surfactant from other similarly charged surfactants.[5] In our preliminary experiments, silica gel and aluminium oxide plates were tested. Thin layer chromatography was developed for separation and identification of different anionic, non-ionic and cationic surfactants.[10] This research focuses on their quantitative determination after chromatographic separation and identification. For this purpose, a potentiometric titration with ion-selective electrodes was tested as a highly automated method that enables very low detection limits for different surfactants.[11]

Experimental

Sample preparation

For the purpose of this work, 1 g of anionic, cationic and non-ionic surfactant standards were investigated: SDS (sodium dodecyl sulphate), HDTMAC (cetyltrimethylammonium chloride) and Kemonecer NI (alkylarylpolyglycolether) were dissolved in 1000 mL of distilled water.

Chromatographic separation

For chromatographic determination, 3 μL of sample standard solutions were spotted with a Pt syringe on 20 · 20 cm glass pre-coated TLC plates with 0.25 mm layers of silica gel 60 F_{254} (Merck, Darmstadt, Germany). Development was carried out in the Camag chromatographic chamber by the ascending technique to the distance of 8 cm with numerous organic solvents and their mixtures with water. Solvent mixtures investigated included: propanol, dichloromethane, ethyl acetate, chloroform, acetonitrile, benzene, tetrachlormethane, buthanole, hexane, and iso-amyl alcohol. After the development, the plates were dried thoroughly and the spots were detected under UV light at $\lambda = 254$ nm.

Qualitative determination

A potentiometric titration applying ion-selective electrode was performed by TITRINO 736 GP, Metrohm, Switzerland. The basis of potentiometric titration was a precipitation titration, in which the analyte was being precipitated with the titrant. All surfactant electrodes were sensitive to both cationic and anionic surfactants. Cationic surfactants were titrated with 0.004 mol L^{-1} anionic titrant, sodium dodecyl sulphate (SDS), at pH 10. Anionic surfactants were titrated with the $c = 0.004$ mol L^{-1} cationic surfactant, Hyamine 1622, at pH 3. Non-ionic surfactants were titrated with $c = 0.01$ mol L^{-1} tetraphenylborate (STPB) at pH 10. Addition of $BaCl_2$ was necessary to compile the non-ionic into the pseudo-cationic surfactant according to eq. (1) and (2), in which NIO represents a non-ionic tenside and NaTPB sodium tetraphenylborate.

$$\mathrm{NIO} + x\,\mathrm{Ba}^{2+} \rightarrow [\mathrm{NIOBa}_x]^{2+} \qquad (1)$$

$$[\mathrm{NIOBa}_x]^{2+} + 2\,\mathrm{NaTPB} \rightarrow [\mathrm{NIOBa}_x]\mathrm{TPB}_{2x} + 2\,\mathrm{Na}^{+} \qquad (2)$$

Results and discussion

Table 1 presents calculated R_F values obtained at the silica gel 60 F_{254^s} plates for a number of chromatographic systems investigated. Detection was performed under UV light (λ = 254 nm), with the fluorescent indicator impregnated within the pre-coated plates. This research does not include application of different reagents for visualization that are proposed in literature[12–18] because detection under UV light is much faster and simpler. R_F values were determined from the recorded plates for all components investigated.

Table 1 – *R_F values obtained on the silica gel 60 F_{254^s} plates*

Tablica 1 – *R_F vrijednosti na podlozi silikagela 60 F_{254^s}*

	Solvent system Sustav otapala	t/min	R_F SDS	R_F HDTMAC	R_F Kemonecer NI
1	CCl_4	13	0	0	0
2	CH_2Cl_2	6	–	–	0.48
3	$C_4H_8O_2$	6	0.88	0.95	0.77
4	C_2H_3N (ACN)	5	0.87	0.92	0.83
5	$C_4H_{10}O$ (BuOH)	39	0.87	0.97	0.75
6	C_6H_6	5	0	0	0.98
7	C_3H_7OH	30	0.65	0.90	0.64
8	$C_5H_{12}O$	55	0.86	0.94	0.66
9	C_6H_{14}	6	0	0	0
10	2-propanol/H_2O	67	0.57	0	–

Developments in the organic non-polar solvents were very fast, but unfortunately, the separations in those systems were not efficient enough. Since the adsorption of the particular surfactant component depends on the present functional groups (surface-active groups), length of the carbon chain in the hydrophobic part and molecular mass of the component, and on the solubility and polarity of the molecules in the stationary and mobile phases, we tested some mixtures of organic solvents with water, but this did not produce better results.

Iso-amyl alcohol was chosen as the best developer for separation and detection of investigated surfactant samples, because it took 55 min for sufficient separation. Since all the components went to the upper part of the chromatographic plate, this system will be further optimized in our subsequent investigations. The best separation of the investigated compounds was obtained on the silica gel 60 chromatographic plates, as presented in Table 2.

Results of the linear range of the surfactant potentiometric titration are presented in Fig. 1–3. Titrations were carried

Table 2 – *Optimal chromatographic procedure for determination of the investigated surfactants*

Tablica 2 – *Optimalni kromatografski proces određivanja ispitivanih površinski aktivnih tvari*

Adsorbent Adsorbens	Solvent Otapalo	Time of development, t/min Vrijeme razvijanja, t/min	Detection Detekcija
silicagel $60F_{254}$s	isoamyl alcohol	55	UV light 254 nm
silikagel $60F_{254}$s	izoamil-alkohol	55	UV-svjetlo, 254 nm

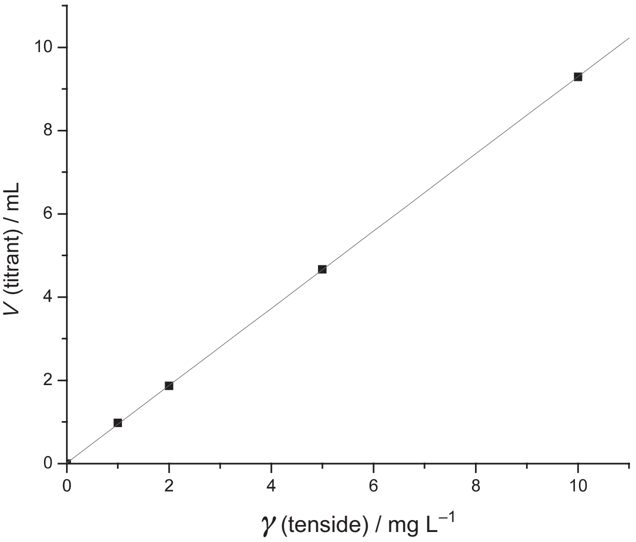

Fig. 1 – *Linear curve for investigated SDS surfactant obtained with ion selective electrode*

Slika 1 – *Baždarni pravac dobiven za površinski aktivnu tvar SDS ($y = 0.927x + 0.0224$, $R^2 = 1.0000$)*

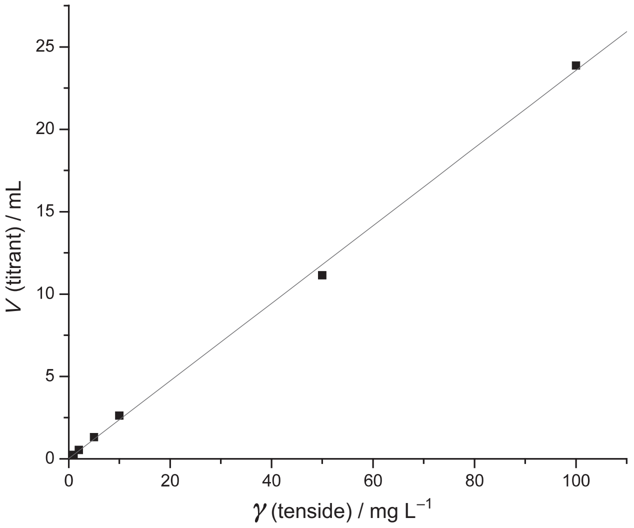

Fig. 2 – *Linear curve for investigated HDTMAC surfactant obtained with ion selective electrode*

Slika 2 – *Baždarni pravac dobiven za površinski aktivnu tvar HDTMAC ($y = 0.2354x + 0.0246$, $R^2 = 0.9988$)*

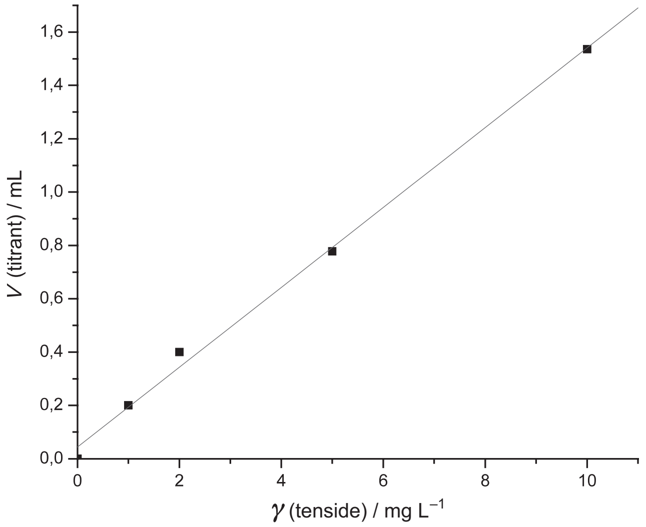

Fig. 3 – *Linear curve for investigated KEMONECER NI surfactant obtained with ion selective electrode*

Slika 3 – *Baždarni pravac dobiven za površinski aktivnu tvar KEMONECER NI ($y = 0.1456x + 0.0876$, $R^2 = 0.9781$)*

out in a dynamic mode, in which the added volume increments were calculated by microprocessor according to the change in electrode potential until the iso-electric point (IEP) was achieved. One of the advantages of this instrumental method is the possible detection of substances in trace amounts. The main criterion for testing the application of potentiometric titration for the surfactants quantitative determination was very low detection and quantification limit. Limits of detection expressed in $\delta = \mu\text{g L}^{-1}$ were in the range from 0.07 (HDTMAC) to 0.26 (SDS) and 0.32 (KEMONECER NI). Linear curves were obtained with very high correlation coefficient for each individual surfactant tested. Potentiometric titration proved to be a very good analytical technique for determination of surfactants present in laundry wastewaters in very low concentrations.

Conclusion

The goal of this investigation was to test two simple and inexpensive methods for identification and determination of anionic, non-ionic and cationic surfactants. To that end, potentiometric titration was used for quantification of surfactants after thin layer chromatographic identification. We found that the best identification and separation solvent system for the investigated surfactants is iso-amyl alcohol on the silica gel 60 F_{254} s adsorbent, detection under UV light of $\lambda = 254$ nm. The quantitative determination follows with the potentiometric titration. These two investigated methods proved to be a very successful combination for anionic, cationic and non-ionic surfactant determination. The advantage of potentiometric titration was its very high degree of automation and very low detection limits obtained with ion-selective electrodes for different surfactants. Thin layer chromatography offered advantages because of its numerous benefits such as low cost, ease of operation, and rapidity of the analysis.

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List of symbols
Popis simbola

c	– concentration, mol L^{-1} – koncentracija, mol L^{-1}
R^2	– correlation coefficient – koeficijent korelacije
R_F	– value at the silica gel plates – vrijednost na podlozi silikagela
t	– time, min – vrijeme, min
V	– volume, mL – obujam, mL
δ	– mass concentration, mg L^{-1} – masena koncentracija, mg L^{-1}
λ	– wavelength, nm – valna duljina, nm

SAŽETAK

Metode za preliminarna određivanja anionskih, kationskih i neionskih surfaktanata

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Danas se različite površinski aktivne tvari (anionske, neionske, kationske i amfoterne) upotrebljavaju u ogromnim količinama u različitim industrijama i domaćinstvima, što čini velik problem za okoliš. Njihova je industrijska primjena proširena na proizvodnju kozmetike, metala, papira i kože, pa se oni zbog toga mogu nalaziti u otpadnim vodama tih industrija u velikim količinama. U Europi se upotrebljava 4 250 000 tona detergenata i 1 190 000 tona omekšivača godišnje. Mnoge od uobičajenih površinski aktivnih tvari imaju izrazito toksično i štetno djelovanje na okoliš i na ljudsko zdravlje, pa su zakonski propisi koji kontroliraju njihovo postojanje u otpadnim vodama dosta strogi: granice za otpuštanje površinski aktivnih tvari u tokove otpadnih voda u Hrvatskoj kreću se u rasponu od δ = 0,05 do 0,10 mg L^{-1}. Na toksičnost i biorazgradivost tih tvari u okolišu utječu mnogi fizikalni, kemijski i biološki čimbenici u međudjelovanju. Kompleksan sastav detergenata u kojima se površinski aktivne tvari miješaju s ostalim komponentama također dovodi do sinergističkog učinka. Nadalje, detergenti odnosno površinski aktivne tvari u njihovom sastavu mogu utjecati na biorazgradivost i toksičnost ostalih komponenata u okolišu. Zbog toga je vrlo važno razviti i primijeniti odgovarajuću a pri tome ne skupu analitičku metodu za određivanje površinski aktivnih tvari u detergentima.

Ovim radom predlažu se dvije jednostavne i brze analitičke metode za određivanje anionskih, kationskih i neionskih površinski aktivnih tvari: tankoslojnu kromatografiju za kvalitativno određivanje te njihovo kvantitativno određivanje potenciometrijskom titracijom s ionsko selektivnim elektrodama. Pokazano je da je najbolja separacija i identifikacija istraživanih komponenata postignuta pomoću razvijača izoamil alkohola na podlozi silikagela 60 F_{254} s, detekcija je provedena pod UV lučnicom pri λ = 254 nm. Nakon kromatografske identifikacije komponenata, obavljena je potenciometrijska titracija surfaktanata uz primjenu različitih ion selektivnih elektroda i titranata (kationski je titriran sa c = 0,004 mol L^{-1} natrij dodecil sulfatiom pri pH 10, anionski sa c = 0,004 mol L^{-1} Hiaminom 1622 kod pH 3, a neionski sa c = 0,01 mol L^{-1} tetrafenilboratom kod pH 10). Te dvije metode pokazale su se kao vrlo dobra kombinacija za određivanje anionskih, kationskih i neionskih površinski aktivnih tvari. Prednost potenciometrijske titracije je visok stupanj automatizacije i vrlo niske granice detekcije koje postižu različite ion selektivne elektrode. Tankoslojna kromatografija također pruža mnoge prednosti nad ostalim analitičkim metodama: niski troškovi, brzina te jednostavnost analize omogućuju uvođenje ove metode u mnoge laboratorije koji se bave analizom detergenata.

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