Simultaneous Determination of Anionic, Amphoteric and Cationic Surfactants Mixtures in Surface Water

IULIANA PAUN*, VASILE ION IANCU, LILIANA CRUCERU, MARCELA NICULESCU, FLORENTINA LAURA CHIRIAC
National Research and Development Institute for Industrial Ecology ECOIND, 71-73 Drumul Podu Dambovitei Str., 060652, Bucharest, Romania

A simple, reliable and accurate HPLC/CAD method was developed for the determination of anionic (sodium dioctyl sulfosuccinate and sodium 1-dodecane sulfonate), amphoteric (CHAPS (3-[(3-Cholamidopropyl) dimethylammonium]-1-propanesulfonate hydrate)) and cationic (benzethonium chloride) surfactants mixture from surface water samples. The chromatographic analysis was performed on an Acclaim Surfactant Plus (150 x 3.0 mm, 3 μm d.p.) column acquired from Thermo Scientific, kept at 30^{0}C. All experiments were performed in gradient elution conditions at a flow-rate of 0.6 mL/min. Mobile phase composition was a mixture of acetonitrile (A) and 0.1 M ammonium acetate solution acidified to pH 5 with acetic acid (B). The limit of detection (LD) were 20 μg/L for anionic surfactants and 30 μg/L for cationic and amphoteric surfactants. The calibration curves were linear between 15 mg/L – 110 mg/L, with R^2 values above 0.992 for all surfactants. Solid phase extraction (SPE) using polymeric (Strata X) cartridges has been applied to extract and concentrate the target analytes from the synthetic samples. Surfactants recoveries after SPE procedure were situated between 91.5÷94.6%. Intra-day and inter-day precision (RSD%) were situated between 4.0 ÷ 7.7% and 7.5 ÷ 11.7%, respectively. Limit of quantitation (LQ) was lower than 80 μg/L for anionic surfactants and 90 μg/L for cationic and 100 μg/L for amphoteric surfactants. The new sensitive and selective HPLC/CAD developed method allows simultaneous determination of anionic, amphoteric and cationic surfactants mixture from environmental samples (surface water).

Keywords: HPLC/CAD, SPE, surfactant, surface water

In industrial terminology, the word detergent is synonymous with surfactant. More precisely, a detergent is a solid or liquid cleaning formulation that contains a number of compounds, one or more of which is a surfactant [1]. Surfactants are found in the composition of a very large number of products. Among the most common are domestic and industrial detergents, pharmaceuticals and cosmetics. They are also used for the solubilization of membranes.

Most commercial products are composed of more than two types of surfactant among four classes: anionic, amphoteric, nonionic and cationic surfactants [2]. Surfactants have an important role in the formation of nanoparticles due to the packing offered by host surfactant assemblies. [3] Anionic surfactants are widely use in production of detergent powders [4, 5].

As the everyday increase in the production of surfactant and their usage, it has become necessary to monitor their levels and impact on different part of the environment. Released into different ecosystems the surfactants are subject to a variety of physical and chemical changes [6].

The analysis of surfactants involves a number of different problems arising from the specificity of this type of sample matrix and analytes (the presence of contaminants, low level of surfactants, their diverse chemical structure, the amphiphilic nature of molecules, limited access to standard solution and reference materials). Attempts to solve these problems involve the use of suitable extraction techniques during the preparation of environmental sample for analysis [7-9].

The extraction techniques used to separate or preconcentrate the surfactants from liquid environmental samples are: liquid-liquid extraction (LLE) and solid phase extraction (SPE). The LLE technique uses high organic solvent consumption and results in toxic wastes while SPE is faster and needs lower sample and solvent volume. For the isolation of surfactants from environmental samples was used solid-phase extraction (SPE) [10-17].

High-performance liquid chromatography (HPLC) is currently the most suitable method for the determination of surfactants. The major advantages of this analytical method are its ability to separate various homologues, oligomers and isomers of complex surfactant mixtures and low detection limits obtained for both charged and uncharged species.

The HPLC analysis of surfactants mixtures, especially of various types, is well known to be very complicated. Reverse phase column RP-18 [12, 18, 19] and RP-8 [11, 20] are used for chromatographic separation of anionic, nonionic, cationic surfactants and their degradation products. Surfactant classes which have chromophore groups are determined by HPLC coupled to ultraviolet (UV) [21, 22] or fluorescence detectors [23, 24]. Because many surfactants have low or no chromophore, universal detector, such as Charged Aerosol Detector (CAD) and evaporative light scattering detector (ELSD) [3, 25], are often used.

The aim of this work was the development and validation of a method using high performance liquid chromatography (HPLC) combined with charged aerosol detector (CAD) for simultaneous analysis of sodium dioctyl sulfosuccinate (anionic surfactant), sodium 1- dodecane sulfonate (anionic surfactant), benzethonium chloride (cationic surfactant) and CHAPS (3-[(3-Cholamidopropyl) dimethylammonium]-1-propane sulfonate hydrate, amphoteric surfactant) in synthetic samples. Chemical structures of these surfactants are shown in figure 1.

---

* *email: iuliana.paun@incdecoind.ro*

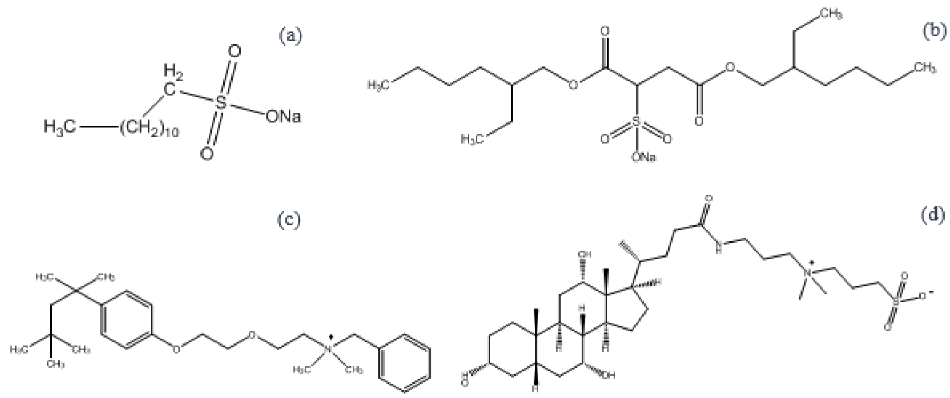


Fig.1. Chemical structures of surfactants: (a) Sodium 1- dodecane sulfonate (anionic surfactant), (b) Sodium dioctyl sulfosuccinate (anionic surfactant), (c) Benzethonium chloride (cationic surfactant) and (d) CHAPS 3-[(3-Cholamidopropyl) dimethylammonium]-1- propane sulfonate (amphoteric surfactant)

Experimental part

Reagents and standard solutions

HPLC grade water was obtained in house using a Milli-Q water purification system (Merck-Millipore). Sodium 1-dodecane sulfonate, sodium dioctyl sulfosuccinate and benzethonium chloride were obtained from Sigma-Aldrich. CHAPS (3-[(3-Cholamidopropyl) dimethyl ammonium]-1-propanesulfonate hydrate), ammonium acetate, HPLC grade acetonitrile and methanol were purchased from Merck.

The stock solutions were prepared by dissolving the surfactants in methanol and bringing them to a final volume of 10 mL with the same solvent. Stock standard solutions were 110 mg/L of sodium 1- dodecane sulfonate, 80 mg/L of sodium dioctyl sulfosuccinate, 92 mg/L benzethonium chloride and 93 mg/L of CHAPS. The standard calibration solutions were made by dilution of the stock standard solutions with mobile phase solutions.

Solid phase extraction procedure

The samples were treated with Dionex Autotrace 280 automated solid-phase extraction apparatus (Thermo Scientific). The extraction applied to the surface water sample was applied to isolate the surfactants from samples.

Solid phase extraction (SPE) was performed using a 6 mL Strata-X (Phenomenex) cartridge packed with a 500 mg sorbent. The cartridges were conditioned with 5 mL of acetonitrile followed by 10 mL of ultra-pure water. Then, the 100 mL sample was loaded at a constant flow rate of 2 mL/min, then the cartridges were washed with 20 mL of ultra-pure water with 10% (v / v) acetic acid and dried 10 min. The retained surfactants were eluted with a mixture of 8.5 L of acetonitrile - 10% (90/10 v / v) acetic acid at a constant flow rate of 1 mL/min. The extract was evaporated and reconstituted in 1 mL of 0.1 M ammonium acetate and transferred to an autosampler vial and analysed.

Instrument and HPLC method: An Ultimate 3000 Liquid Chromatograph (Thermo Scientific) consisting of a quaternary pump, a thermostatic column compartment, an autosampler and a UV-VIS array detector coupled in tandem with the Corona Veo RS Load Detector. Chromatographic analysis was performed on the Acclaim Surfactant Plus (3.0 x 150 mm, 3 pm) column of Thermo Scientific which was maintained at 30°C for 15 min. All experiments were carried out under gradient elution conditions at a flow rate of 0.6 mL / min. The mobile phase composition was a mixture of acetonitrile as eluent A and 0.1 M aqueous ammonium acetate acidified to *p*H 5 with acetic acid as eluent B. The gradient elution program is given in table 1. The injection volume of the sample was 5 μL.

Charged aerosol detection (CAD) is a mass sensitive technique for determining levels of any non-volatile and many semi-volatile analytes after separation by HPLC. The detection method involves pneumatic nebulization of HPLC column eluent, exclusion of the largest droplets via an impactor, and ambient solvent evaporation to form an aerosol of analyte particles. A turbulent jet of positive ions, formed by passing a secondary stream of gas by a corona discharge and through an orifice, is mixed with the opposing analyte aerosol stream. In this process, charge is transferred diffusional to analyte particles. Excess positive ions are trapped by a weak electric field and charged particles are pushed through a conductive filter, which

Time (min)	Acetonitrile (A) %	0.1M Ammonium Acetate,(B)%
-8	25	75
10	80	20
13	80	20

Table 1

GRADIENT ELUTION PROGRAM USED TO SEPARATE THE FOUR SURFACTANTS

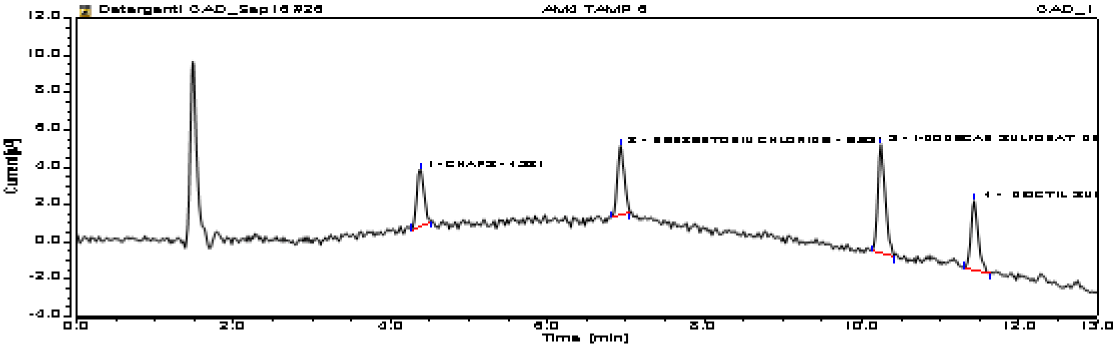


Fig. 2. Chromatogram of 50 mg/L surfactants standard solution

transfers the charge to an electrometer for signal transduction. The signal was generated in direct proportion to the quantity of substance. The CAD nebulizer was set at ambient temperature and the evaporator tube to 30°C, also the filter constant was set to 3.6 s.

The data and results were recorded using Chromeleon 7.2 software acquired from Thermo Scientific together with the HPLC system.

The Chromatogram of mixture standard solution in ammonium acetate 0.1M obtained in these conditions is presented in figure 2. The retention time and peak area of the surfactants is given in table 2.

Results and discussions

Validation experiments

The method was validated for surface water considering the following parameters: selectivity, linearity, detection limits and quantitation limits, intra-day and inter-day precision, accuracy and recovery.

Linearity, this parameter was studied over the calibration curve which was obtained by analyzing standard solutions at five concentrations between 15 mg/L and 80mg/L for sodium dioctyl sulfosuccinate (anionic surfactant), between 20.6 mg/L and 110 mg/L for 1 dodecane sulfonate sodium (anionic surfactant), between 17.4 mg/L and 92 mg/L for benzethonium chloride (cationic surfactant) and between 17.4 mg/L and 93 mg/L for CHAPS (3-[(3-Cholamidopropyl)dimethylammonio]-1-propanesulfonate hydrate, amphoteric surfactant).

Detection limits (LOD) and quantitation limits (LOQ) were calculated using the calibration curve for each surfactant. Sensitivity and linearity of the detector response to each surfactant was assessed by the calibration curves obtained from a series of five standard solutions figure 3. The correlation coefficient value obtained for each surfactant was higher than 0.99.

The sensitivity of this HPLC method was determined using limits of detection and quantitation. LOD is the lowest analyte concentration detectable by HPLC for the proposed method. On the other hand, the LOQ is the lowest concentration that can be quantified accurately by the proposed method.

For *intra-day* method precision, ten replicates were spiked, extracted and analyzed in the same day, while for *inter-day* method precision, the extraction and analysis were performed for three replicates, in four days.

Individual recoveries for overall analytical procedure were determined by spiking surface water with working standard mixture which contained 110 mg/L of sodium 1-dodecane sulfonate, 80 mg/L of sodium dioctyl sulfosuccinate, 92 mg/L benzethonium chloride and 93 mg/L of CHAPS.

Table 2

RETENTION TIMES AND PEAK AREA OF THE SURFACTANTS

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount mg/L
1	CHAPS	4.381	0.338	3.040	19.25	18.60	14.2917
2	BENZENTHONIUM CHLORIDE	6.931	0.375	3.721	21.37	22.77	13.7760
3	SODIUM 1 DODECANE SULFONATE	10.242	0.637	5.840	36.30	35.74	17.3687
4	SODIUM DIOCTYL SULFOSUCCINATE	11.429	0.405	3.740	23.08	22.89	12.1058

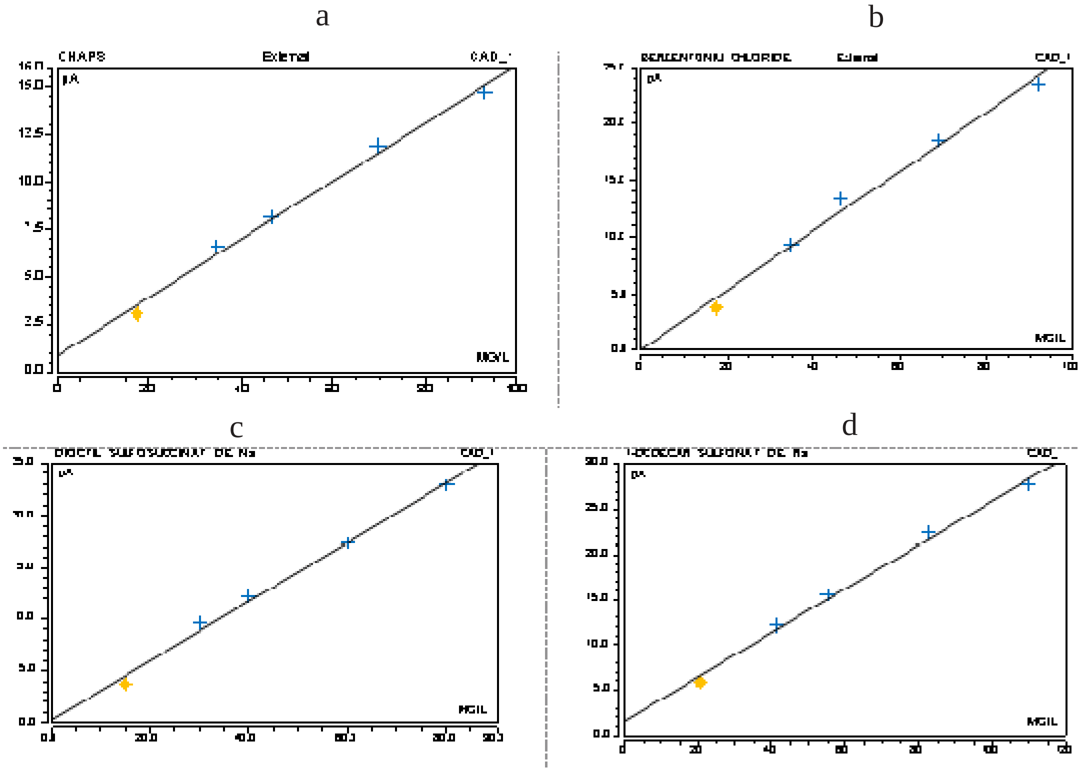
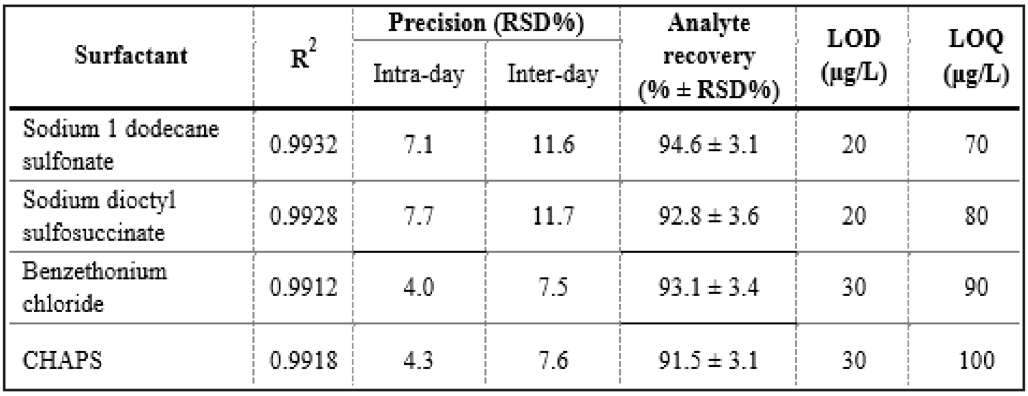


Fig. 3. Calibration curve for (a)CHAPS, (b) benzenthonium chloride, (c) sodium dioctyl sulfosuccinate and (d) sodium 1- dodecane sulfonate



Surfactant	R^2	Precision (RSD%)		Analyte recovery (% ± RSD%)	LOD (μg/L)	LOQ (μg/L)
		Intra-day	Inter-day			
Sodium 1 dodecane sulfonate	0.9932	7.1	11.6	94.6 ± 3.1	20	70
Sodium dioctyl sulfosuccinate	0.9928	7.7	11.7	92.8 ± 3.6	20	80
Benzethonium chloride	0.9912	4.0	7.5	93.1 ± 3.4	30	90
CHAPS	0.9918	4.3	7.6	91.5 ± 3.1	30	100

Table 3
THE VALIDATION PARAMETERS FOR THE PROPOSED METHOD: CORRELATION COEFFICIENTS (R^2), INTRA-DAY AND INTER-DAY PRECISION, ANALYTE RECOVERY, LIMITS OF DETECTION AND LIMITS OF QUANTITATION

Obtained chromatographic validation data are presented in table 3.

Determination of surfactants from surface water samples

The proposed HPLC-CAD method was applied for the determination of Sodium dioctyl sulfosuccinate (anionic surfactant), 1 dodecane sulfonate sodium (anionic surfactant), benzethonium chloride (cationic surfactant) and CHAPS (3-[(3-Cholamidopropyl) dimethylammonio]-1-propanesulfonate hydrate, amphoteric surfactant) from five surface water samples from Danube River and tributary Jiu River at the entrance to the drinking water treatment plant of five cities. None of the four surfactants analysed was detected.

Conclusions

The new sensitive and selective HPLC/CAD developed method allows simultaneous determination of anionic, amphoteric and cationic surfactants mixture from environmental sample (surface water, wastewater). This proposed method was validated in terms of linearity, precision, accuracy, detection and quantitation limits. The method was linear over the concentration range between 15-80 mg/L for sodium dioctyl sulfosuccinate (anionic surfactant), 20.6-110 mg/L for 1 dodecane sulfonate sodium (anionic surfactant), 17.4-92 mg/L for benzethonium chloride (cationic surfactant) and between 17.4-93 mg/L for CHAPS (3-[(3-Cholamidopropyl) dimethylammonio]-1-propanesulfonate hydrate, amphoteric surfactant). Good surfactant recoveries after SPE procedure were obtained for each compound: 92.8% for sodium dioctyl sulfosuccinate (anionic surfactant), 94.6% for 1 dodecane sulfonate sodium, 93.1% for benzethonium chloride and 91.5% for CHAPS (3-[(3-Cholamidopropyl) dimethylammonio]-1-propanesulfonate hydrate). The good recovery values (>90%) shows that the method is accurate. Intra-day and inter-day precision (RSD%) were situated between 4.0 ÷ 7.7% and 7.5 ÷ 11.7%, respectively. Low limits of detection were obtained for all surfactants (20 μg/L - 30μg/L).

References

1. MORELLI, J.J., SZAJER, G., J. Surfactants Deterg., **3**, no.4, 2000, p. 539.
2. HUTANU, F., BADEA, D.M., MUNTEANU, C., PETRESCU, S., MARCU, M., Rev. Chim. (Bucharest), **65**, no. 1, 2014, p. 40
3. SIMONESCU, C.M., TEODORESCU, V.E., CAPATINA, C., Rev. Chim. (Bucharest), **59**, no. 12, 2008, p. 1327
4. IM, S.H., JEONG, Y.H., RYOO, J.J., Anal. Chim. Acta, **619**, 2008, p. 129
5. POPA, G.A., POPA (ENACHE), D.F., SLAVE (CLEJ), D.D, SPIRIDON, I.D., MIREA, C.M., CIOCANEA, A., Rev.Chim. (Bucharest), **68**, no. 1, 2017, p. 6
6. OLKOWSKA, E., POLKOWSKA, Z., NAMIESNIK, J., Talanta, **88**, 2012, p. 1
7. OLKOWSKA, E., POLKOWSKA, Z., NAMIESNIK, J., Talanta, **116**, 2013, p. 210
8. PETRE, J., GALAON, T., IANCU, V.I., VASILE, G.-G., STANESCU, E., PASCU, L.F., SIMION, M., CRUCERU, L., Rev. Chim. (Bucharest), **67**, no. 8, 2016, p. 1436
9. GALAON, T., PETRE, J., IANCU, V.I., CRUCERU, L., VASILE, G., PASCU, L.F., LEHR, C.B., Rev. Chim. (Bucharest), **67**, no. 8, 2016, p. 1474
10. MATTHIS, E., HOLT, M.S., KIEWIET, A., RIJS, G.B.J., Environ. Toxicol. Chem., **18**, 1999, p. 2634
11. MERINO, F., RUBIO, S., PERE-BONDINO, D., Anal. Chem., **76**, 2004, p. 3878
12. BASSARAB, P., WILLIAMS, D., DEAN, R., LUDKIN, E., PERRY, J., J. Chromatogr. A, **1218**, 2011, p. 673
13. CASSTILLO, M., VENTURA, F., BARCELO, D., Waste Manage. **19**, 1999, p. 101
14. CASSTILLO, M., ALONSO, M.C., RIU, J., BARCELO, D., Environ. Sci. Technol., **33**, 1999, p.1300
15. HENNIO,N M.C., J. Chromatogr. A, **856**, 1999, p. 3
16. NUNEZ, O., MOYANO, E., GALCERAN, M.T., J. Chromatogr. A, **946**, 2002, p. 275
17. PICO, J., FONT, G., MOLTO, J.C., MANES, J., J. Chromatogr. A, **885**, 2000, p.251
18. LARA-MARTIN, P.A., GOMEZ-PARRA, A., GONALEZ-MAZO, E., J. Chromatogr. A, **1137**, 2006, p.188
19. RICO-RICO, A., DROGE, S.T.J., WIDER, D., HERMENS, J.L.M., J. Chromatogr. A, **1216**, 2009, p. 2996
20. LEON, V. M., GONALEZ-MAZO, E., GOMEZ-PERRA, A., J. Chromatogr. A, **889**, 2000, p. 211
21. VEJRUP, K. V., WOLOFF, P., Sci. Tot. Environ., **300**, 2002, p. 51
22. MIYAUCHI, T., MORI, M., ITO, K., Chromatogr. A, **1095**, 2005, p. 74
23 SCULLION, S. D., CLENCH, M. R., COOKE, M., ASHCROFT, A.E., Chromatogr. A, **733**, 1999, p. 207
24. SABLAYROLLES, C., MONTREJOUD-VIGNOLES, M., SILVESTRE, J., TREILHOU, M., Int. J. Anal. Chem., 2009, 2009, p.1
25. ESCRIG-DOMENECH, A., SIMO-ALFONSO, E. F., RAMIS-RAMOS, G., Anal. Chim. Acta, **932**, 2016, p. 106

Manuscript received: 11.11.2017