Continuous system with microwave irradiation to obtain alkyl benzoates

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Abstract

In this study, a continuous linear alcohol derivatization is developed. Reaction of alcohol group (ROH) with benzoyl chloride (BC) is carried out in an on-line system with UV detection. All reaction conditions, as flow rate (FR), ROH/BC molar ratio, wavelength, temperature, microwave (MW) irradiation and reaction coil size (internal diameter and length) were optimized. 0.5 mL min^{-1}, 2.49 [BC]/[ROH], 230 nm, 60 °C or medium power (225 W) when MW irradiation was used and a reactor coil of 159 μL (0.5 mm × 810 mm) were the optimum conditions. The on-line system with microwave irradiation was more efficient than the one with a water bath heating. The developed system reduces analysis time consumption, reagent amounts and this system was used to evaluate the composition of commercial samples of alcohols polyethoxylated (surfactants).
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1. Introduction

There are alcohol compounds with industrial importance, as non-ionic ethoxylated surfactants (i.e. alcohol ethoxylates), which became popular since they are more friendly to the environment than most other surfactants [1,2]. The analysis of these surfactants has been performed by several chromatographic methods [3–8]. However, a simple method, for the quantification of these compounds in the commercial mixtures is required. The spectrophotometric techniques could be an excellent alternative; however the lacks of chromophore groups are a problem which could be faced by using derivatization technique.

This derivatization technique has received special attention because it enables highly sensitive detection of these alcohol compounds by bonding a chromophore group that results in products with a strong UV absorption. Phenyl isocyanate and benzoyl chloride (BC) reagents have been reported for PAS derivatization under conventional conditions [5]. On the other hand, microwave (MW) heating can advantageously replace

classical heating by allowing (i) a close fit of the irradiation mode (continuous or sequential) with each reaction medium; (ii) efficient control of the given energetic power and (iii) the development of strong temperature gradients, leading to a noticeable shortening of reaction times, in particular for the more reactive aromatic substrates. As a matter of fact, in publications concerning to MW technology, a growing number of patents for chemical synthesis are appearing [9–14]. However, scale-up batch processes are hampered by problems, such as the homogeneity of the electromagnetic field in the reactor. For these reasons, the technology of using MW heating for chemical synthesis is not yet larger reaction volumes.

The advantage of MW heating over conventional heating is that the reaction mixtures absorb the energy directly. Thus, the temperature gradient rises steeply, leading to an acceleration of the reaction, an essential condition in a flow-through system [12–18]. Another important advantage of MW heating in such system is the "on/off condition", i.e. the possibility to turning the MW source on or off instantaneously. This allows carrying out MW irradiation in a sequential mode. The aid of this work was to develop a FIA system for the derivatization of linear alcohol (ROH) and PAS using microwave irradiation and UV detection. The reaction conditions for the benzoyl chloride were

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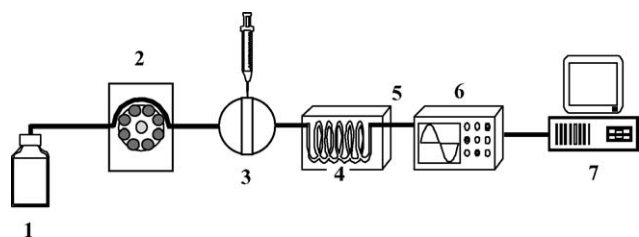*E-mail address:* caceresana7@cantv.net (A. Cáceres).

Fig. 1. Manifold of the continuous microwave irradiation FIA–UV on-line system. (1) Solvent carrier (MeCN), (2) peristaltic pump with tubing of 0.89 mm and 0.5 mL min^{-1}, (3) injection valve (loop of 50 μL), (4) coil reactor of 379 μL (193 cm) and 0.5 mm of internal diameter, (5) microwave oven at different power: high (450 W), medium (225 W) and lower (112 W), or water bath at 60 °C, (6) PDA–UV detector and (7) computer.

established. The continuous microwave reactor (CMWR) coupled with UV detection provided high sensitivity reducing the amount of reagent and reducing analysis time. The developed method system was applied to real samples of PAS.

2. Experimental

2.1. Solvent and reagents

Linear alcohols (C$_n$OH with n = 9, 12, 14 and 16 carbon atoms number) were used (Merck, 98%). The studied PAS samples were as follows: AE*X* (ethoxyl, Arch Chemical) and LA*X* (Clariant, France) which are mixtures of linear primary C$_{12}$, C$_{14}$ and C$_{16}$ fatty alcohol polyethoxylates and *X* is the ethylene oxide number (EON). The derivatized agent used was benzoyl chloride (Merck, 99%). Acetonitrile (MeCN) used was HPLC grade from J.T. Baker Chemicals.

2.2. Apparatus

FIA derivatization system consisted of a peristaltic pump, model mini-S 840 (30 rpm) from Ismatec, a Rheodyne injection valve model 5020. Domestic microwave oven and spiral Teflon coil with different lengths and internal diameter were used. The manifold used is shown in Fig. 1. The injection valve was filled up with a solution containing BC and linear alcohol in MeCN. By switching the injection valve, loop content was inserted into the MeCN carrier stream. Finally the linear alcohol products were detected by UV.

3. Results and discussion

3.1. Reaction conditions

A preliminary study to select the optimum wavelength was made. The product was synthesized using a conventional method [1]. This method presented several disadvantages: a long time of reaction (1 h at 60 °C), high consumption of reagents and high exposition to the reagents among others problems. *n*-Nonanol was selected in order to keep a patron.

3.1.1. Wavelength

The spectral scan from 200 to 700 nm was carried out for a solution (50 mM each one) of the pure nonyl benzoate (alcohol
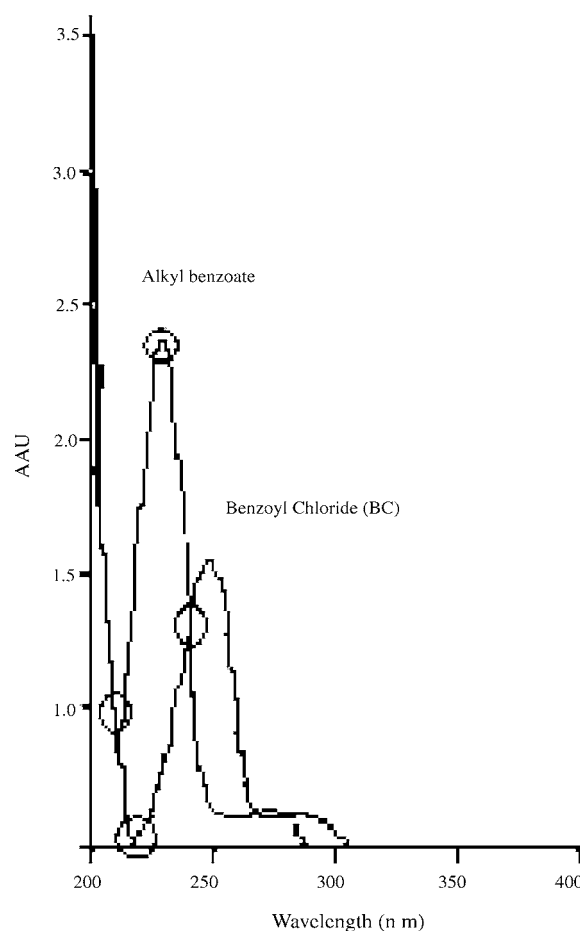

Fig. 2. Spectrums of BC (50 mM) and the alkyl benzoate (50 mM) at 25 °C, solvent: MeCN.

product) and the benzoyl chloride which is the reference solution. Maximum peak at 248 and 235 nm were obtained for BC and the alcohol product. These results are in agreement with the reported information [19]. Fig. 2 shows both spectral, marked points represented the wavelength selected for following studies (215, 225, 230 and 235 nm). The selection of the optimum one was based on the bigger difference between reference solution (BC) and the reaction mixture (alcohol product). After comparison of the four wavelengths (Fig. 3), 230 nm was the one where the difference between the BC and alcohol product was bigger. This wavelength was used for the followed experiences.

3.1.2. Molar ratio

After the optimum wavelength was selected, solutions of different molar ratio were analyzed using the on-line system; [BC]/[ROH] was optimized until the greater conversion was obtained. A benzoyl chloride reference solution was scanned, to determine the difference between the signals of the alcohol product and the BC. Fig. 4 shows the fiagrams of each [BC]/[ROH] assayed and BC reference solution. The higher signal difference was obtained when [BC]/[ROH] was 2.49. It means that the excess of BC makes to react most of the ROH present. BC concentration was kept constant due to this compound has a strong absorption in the UV region.
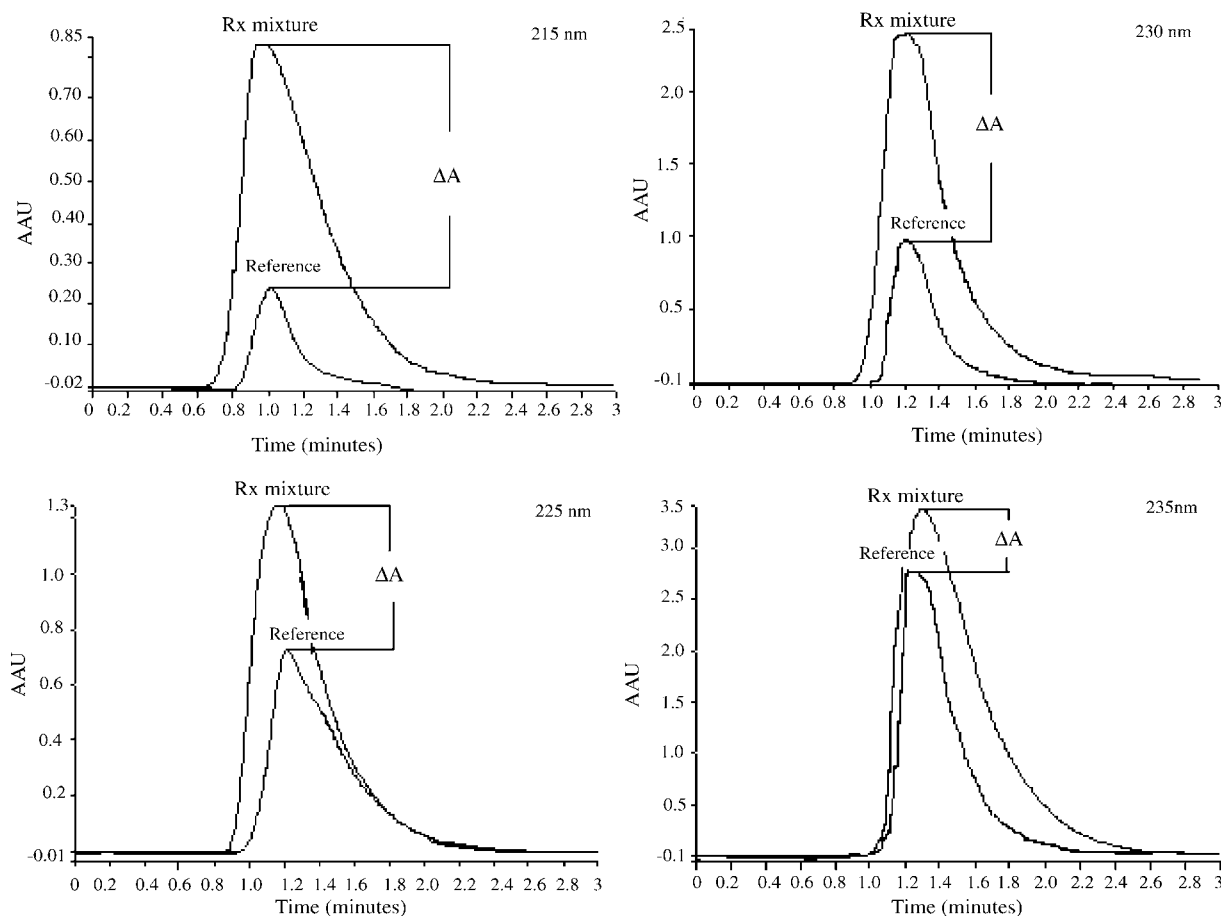
Fig. 3. Diagrams of the four evaluated wavelengths: 215, 225, 230 and 235 nm in the continuous system. Conditions: molar ratio [CB/OH] = 2.42; flow rate, 0.5 mL min^{-1}; temperature, 60 °C (water bath); coil reactor of 379 μL (193 cm) and 0.5 mm internal diameter.

3.2. Continuous system

3.2.1. Flow rate (FR)

Under the same conditions four different flow rates were used, signal intensity (mAU) of 220, 200, 180 and 150 were
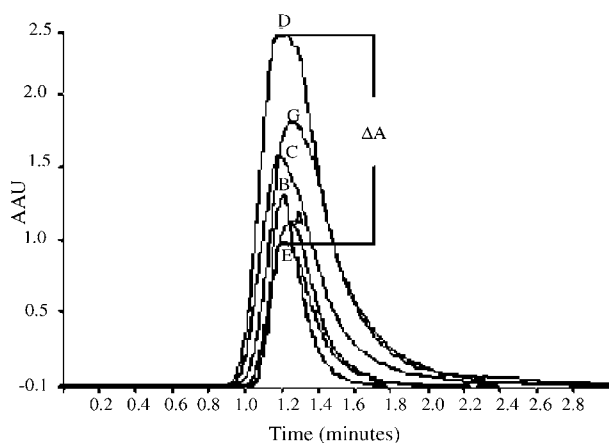

Fig. 4. Fiagrams of reaction mixture and reference using the following molar ratios [CB/OH]: A, 12.45; B, 4.79; C, 3.11; D, 2.49; G, 1.66 and E, reference solution. Conditions: flow rate, 0.5 mL min^{-1}; temperature, 60 °C (water bath); Teflon reactor of 379 μL (193 cm) and 0.5 mm internal diameter; wavelength, 230 nm.

obtained for 0.2, 0.5, 1.0 and 1.5 mL min^{-1}, respectively. At low FR (0.2 and 0.5 mL min^{-1}) higher intensity was obtained, however, peak widths of 2.5 and 1.5 min were obtained at 0.2 and 0.5 mL min^{-1}, respectively. As broader peaks were obtained with 0.2 mL min^{-1}, a FR of 0.5 mL min^{-1} was selected as the optimum flow rate, moreover, thinner peaks let to increase the number of samples per hour (sample throughput).

3.2.2. Comparison of the use of water bath and microwave irradiation

Initially, a water bath at different temperatures (25, 40, 50, 60 and 70 °C) was used. At higher temperature, signal intensity increased (Fig. 5a); however after 60 °C bubbles problems were observed, for this reason 60 °C was selected as the optimum temperature. For this experiment a reactor of 193 cm was used (379 μL).

The effect of MW irradiation on the derivatization reaction was evaluated. When high power (450 W) was used the signal intensity increases, however signal fluctuations were observed, they could be because of the bubbles formation. When medium power (225 W) was used there were no fluctuations and signal intensity was high. Fig. 5b shows a comparison of two reactors, the first one (193 cm or 379 μL) was the optimum when a water bath was used and the second one (83 cm, 159 μL) was essayed in order to reduce the dispersion obtained with the previous

(a) **Water bath**

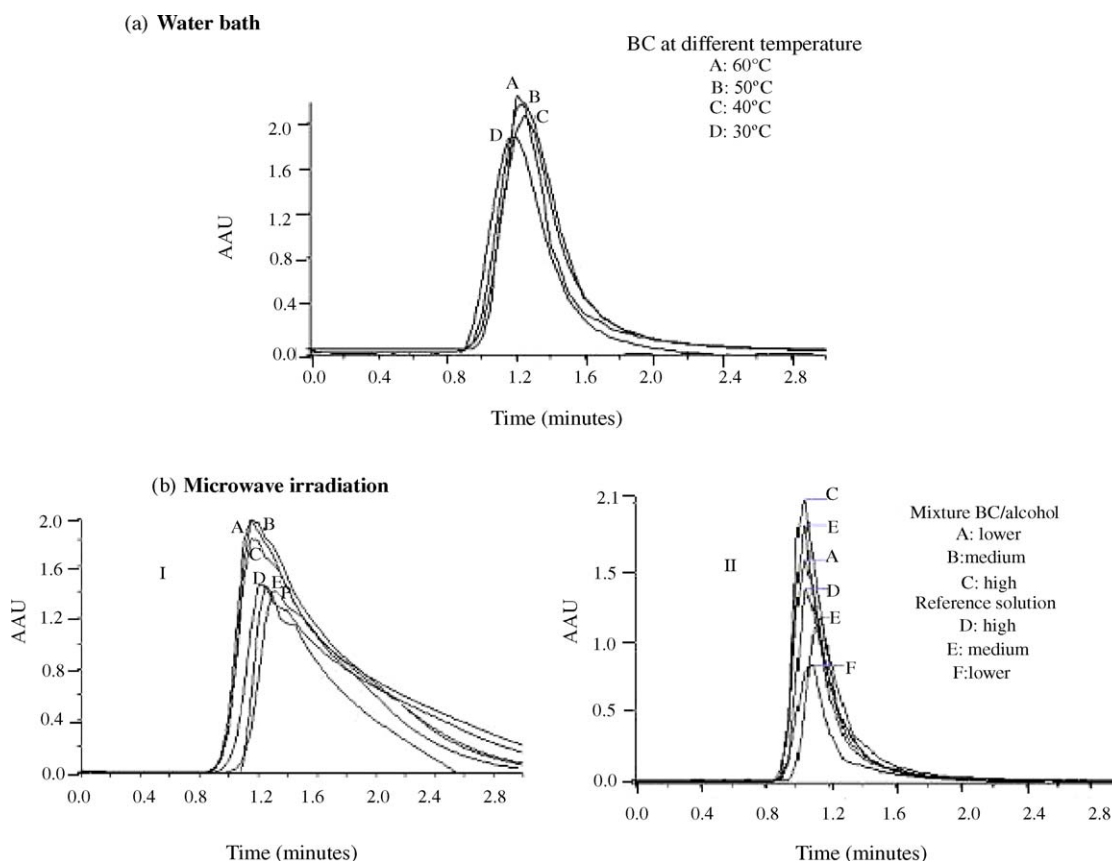
(b) **Microwave irradiation**

Fig. 5. (a) Optimization of the reaction temperature using water bath at 25, 40, 50 and 60 °C. (b) Effect of the microwave irradiation at different power A: high (450 W), B: medium (225 W), C: low (112 W) for the reaction mixture and D–F correspond to high, medium and low power for the reference solution using (I) coil reactor of 379 μL (193 cm) and (II) coil reactor of 159 μL (81 cm). Conditions: wavelength, 230 nm; molar ratio [BC/OH] = 2.49 and flow rate, 0.5 mL min^{-1}.

one. When the two fiagrams are compared it is clear to see the improvement obtained when MW irradiation was used, the analysis time was reduced (almost two times).

3.2.3. Reactor size
3.2.3.1. Length. Three lengths were evaluated, 193, 81 and 35 cm. The results showed that as length of coil reactor decrease, dispersion and signal intensity decrease, with short irradiation time, smaller percentage of products are obtained. The optimum length was 81 cm (159 μL using MW irradiation).

3.2.3.2. Internal diameter. It is well known that when internal diameter decreases, the dispersion of the system is reduced; nevertheless, the higher diameter reactors increase the contact of sample and carrier reagent as well as the reagents consumption. Reactors of different internal diameters were evaluated: 0.25, 0.5 and 0.8 mm i.d. The results (Fig. 6) show that the reactor of 0.5 mm of internal diameter provides the best commitment between intensity and dispersion.

3.2.3.3. Number of turns (NT). As it is wider known when, the same length and internal diameter of Teflon tubing is used the number of turns (turns around the reactor coil support) could influence in the signal intensity for this reason three NT were evaluated. Signal intensity (mAU) of 92.55, 224.82 and

297.77, were obtained with 10, 20 and 30 turns, respectively. The higher intensity was obtained when 30 turns were used; due to the reaction is accelerated with the increasing of NT [20].

3.3. Analytical characteristics

Analytical characteristics of the system are shown in Table 1. The detection limit (DL) was calculated as the concentration value corresponding to three times the standard deviation (σ) of

Table 1
Analytical characteristics of FIA system ($n = 10$)

Parameter	C$_{12}$	Mixture (C$_{12}$, C$_{14}$ and C$_{16}$)
Linear range (mg L^{-1})	20–200	20–200
Detection limit (mg L^{-1}), 3σ	0.021	0.006
Quantification limit (mg L^{-1}), 10σ	0.025	0.008
Regression equation	$y = 0.37346x$ $+ 0.00724$	$y = 0.91279x$ $- 0.00393$
Correlation coefficient	0.9966	0.9967
Sample throughput (sample h^{-1})	56	56
Average accuracy (%)	17.87	4.48
Average precision (R.S.D.%)	0.75	0.67

Table 2
Results of five samples analyzed using the continuous system developed and comparison of the two calibration graphs used

Sample	Expected [ROH][a]	Found [ROH][a]		E_1[b]	E_2[b]
		Mixture calibration curve	$C_{12}OH$ calibration curve		
AE4	95 ± 5	92.48 ± 1.40	74.83 ± 3.12	2.60	21.23
AE10	95 ± 5	98.68 ± 1.85	83.28 ± 2.14	3.87	12.34
AE18	95 ± 5	86.52 ± 2.03	66.71 ± 3.23	8.92	24.80
LA4	98 ± 2	99.03 ± 1.11	91.27 ± 1.78	1.05	6.87
LA7	98 ± 2	92.15 ± 1.89	74.38 ± 0.93	5.97	24.10

[a] Percentage of alcohol surfactant.
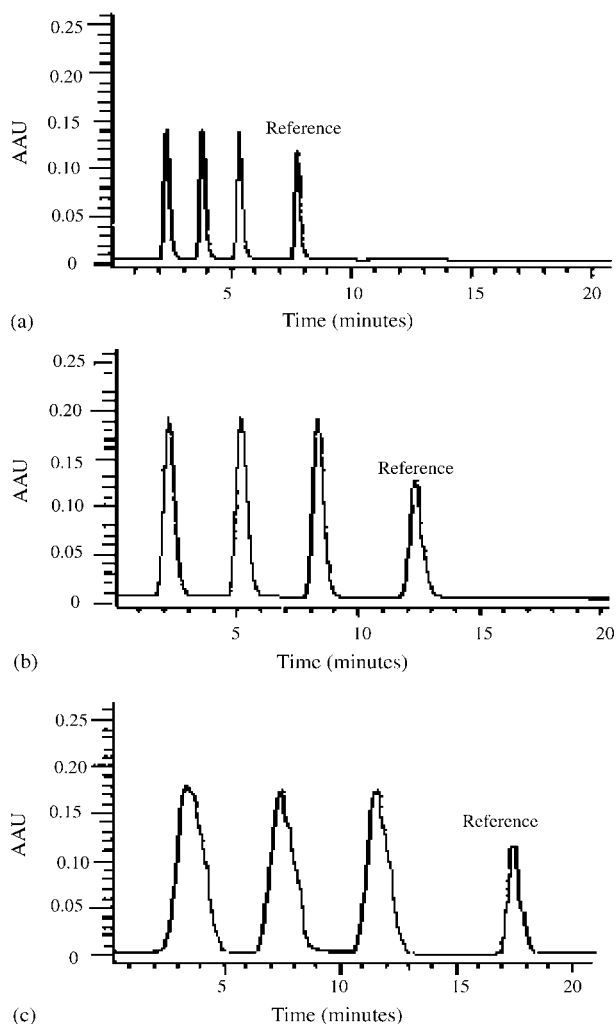[b] Absolute error between the expected and the found ROH concentration.

Fig. 6. Fiagrams of the reaction mixture and the reference solution using a coil reactor of 159 μL with different internal diameters: (a) 0.25 mm; (b) 0.5 mm and (c) 0.8 mm. Conditions: microwave irradiation at medium power; molar ratio [CB/OH] = 2.49; wavelength, 230 nm and flow rate, 0.5 mL min^{-1}.

concentration is calculated using the mixture solution the value is closer to the real one. However, when the pure $C_{12}OH$ calibration graph was used the values were distant of the expected one. The difference of this calculated value is due to the molar absorptivity which decreases with the chain length. Results show that this method can be used for quantification of commercial samples of alcohol polyethoxylated with acceptable result for industrial propose. Disparity between expected and found linear alcohol concentration was <5% (see Table 2), when a calibration curve of alcohols mixture (E_1) and $C_{12}OH$ (E_2) was used.

4. Conclusions

The developing continuous alcohol derivatization system allows to carry out the reaction, reducing the amount of reagents as well as the analysis time. The used of MW irradiation resulted in improvement of reaction. The system was applied to real samples of alcohol polyethoxylated showing a good agreement with the expected results.

10 measurements of the blank solution (DL = 3σ), and the quantification limit (QL) was calculated as the concentration value corresponding to 10σ. In general, the developed method shows an excellent precision, relative standard deviation (R.S.D.) <3% was observed (Section 3.4).

3.4. Analysis of surfactants samples using the on-line system

A calibration curve of $C_{12}OH$ from 20 to 200 mg L^{-1} was prepared. This linear dynamic range is specific for each alcohol. The commercial samples of alcohol ethoxylated surfactant were evaluated by quantification of the $C_{12}OH$ content in these samples. These commercial samples are a mixture of alcohol polyethoxylated in which the higher proportion is $C_{12}OH$ while C_{14} and C_{16} are the lower proportion. For this reason two calibration graphs were built. The first one was made with 50% of $C_{12}OH$, 30% of C_{14} and 20% of C_{16}, and the second one was prepared only with $C_{12}OH$. Table 2 shows that when sample

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