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Talanta 66 (2005) 118–124

Talanta

www.elsevier.com/locate/talanta

Simultaneous determination of three surfactants and water in shampoo and liquid soap by ATR-FTIR

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Received 30 January 2004; received in revised form 18 October 2004; accepted 19 October 2004
Available online 8 December 2004

Abstract

It is demonstrated for the first time that the principal constituents of a shampoo as well as of a liquid soap –three surfactants and water– can be determined directly, simultaneously and quickly in undiluted samples by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy in the middle infrared region, despite the broad absorption bands of the solvent. Two of the surfactants, sodium lauryl ether sulfate (SLES) and cocoamidopropyl betaine (CAPB), are common to both formulations; alkylpolyglucoside (APG) is the third surfactant of the liquid soap and cocodiethanolamide (CDEA), the corresponding ingredient of the shampoo. Absorbance data of the undiluted samples and of the calibration standards was collected in the middle infrared region of the spectrum (800–1600 and 1900–3000 cm^{-1}). Two methods of multivariate quantification were compared: classical least squares (CLS), where absorbance data measured at 200 wavenumbers was processed, and inverse least squares (ILS), where data at 10 selected wavenumbers was analyzed. A spectra normalization procedure, based on a dominating water band, was examined. Twenty-seven standard mixtures were used for each application, consisting of all combinations at three concentration levels of each surfactant, respectively the lower limit, the expected value and the upper limit accepted in quality control. By favoring wavenumbers where absorption bands of the minor components (APG in the liquid soap and CDEA in the shampoo) are more intense, good results were obtained for 18 simulated samples of shampoo and 18 samples of liquid soap, no matter if calculations were made by CLS or ILS. The relative errors for water (major component, 84–88%) and SLES (7–10%) were always below 2%; for CAPB (2–4%), APG (<2%) and CDEA (<2%), they occasionally reached 5% of the component, an uncertainty of less than 0.07% in terms of the sample weight.

Keywords: Fourier transform infrared spectroscopy (FTIR); Attenuated total reflection (ATR); Spectrophotometry; Multivariate analysis; Surfactant analysis; Water determination

1. Introduction

Absorption spectroscopy in the middle infrared region is used universally for characterization purposes, taking advantage of the distinctive molecular vibrational bands of organic (and inorganic) groups in this region. In comparison with spectrophotometry in the UV–vis region, based on electronic transition bands, selectivity is usually much higher, but due to short pathlengths typical in transmittance or reflectance IR of liquids, the measured absorbances are lower; also, the instrumentation required is more expensive and the otherwise universal solvent – water – presents broad interfering absorption bands, some factors restraining the application in quantitative analysis. Popularization of interferometric Fourier transform infrared (FTIR) instruments interfaced to increasingly powerful microcomputers that run the fast Fourier transform algorithm (developed in the 1970s) has removed some of these restrictions. These instruments have much lower acquisition and maintenance prices than classical dispersive IR spectrometers, are more compact, stable and reliable, reduce the time to obtain a spectrum from minutes to seconds and store and manipulate data digitally (e.g., subtraction of water or other background bands, sum-

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doi:10.1016/j.talanta.2004.10.005

mation of spectra to improve the signal/noise ratio, etc.) [1–6].

The commercial availability of FTIR equipment accessories for measurements in the reflectance mode is another important advance. In the attenuated total reflectance (ATR) mode, also known as internal reflectance, the beam is directed onto the interface of the transparent window material, usually ZnSe (water resistant), at an incidence angle that results in "total" reflection. In fact, the evanescent wave of the reflected radiation interacts with the sample molecules exposed on the window surface, attenuating the "total" reflection at the wavenumbers corresponding to absorption bands of the sample [9]. This technique is not very suitable for the determination of trace components since the "optical path" is minimal ($\approx 10^{-5}$ m). To overcome the lack of sensitivity, multiple reflection ATR devices have been developed, sometimes with a diamond window to improve chemical and mechanical resistance in routine use. Compared to the transmittance cell, the ATR mode simplifies and minimizes sample handling and allows spectra from opaque samples to be recorded directly [7,8]. Typically, a drop of sample is simply spread over the horizontal surface; the film thickness is irrelevant and the cleanup of the scratch-free diamond surface by wiping-off the sample with a solvent is quick and easy.

With these relatively favorable characteristics, FTIR-ATR is finding its way in quantitative analysis, and the number of methods is progressively growing, embracing samples like polymers, pharmaceutical products and petrol components [10–15]. However, to the best knowledge of the authors, quantitative applications of FTIR-ATR to surfactants have not yet appeared in the literature. This class of compounds is very important and amply used in the formulation of industrial, household and cosmetic products where, frequently, two or more distinct surfactants are combined. The need for quantitative analysis starts with the raw materials, turns crucial during manufacturing and filling processes and may reach the shelf, under scrutiny of the producers or regulatory agencies.

Although the control of raw material is of great value and comprises, perhaps, a fertile field for straightforward applications of FTIR-ATR, to demonstrate the potentiality of this technique in more relevant and complex situations, the authors have chosen to investigate the simultaneous determination of various surfactants in shampoos and liquid soaps. The surfactants are the active ingredients in both products, being responsible, in a simplified view, for the removal of grease and dirt from the hair and skin. The combination of surfactants, each of them with a different function (and price!), depends on the application and the expected performance. The main surfactant in both formulations, for the brand used as a model-product (similar to commercial products), is sodium lauryl ether sulfate (SLES, Fig. 1), an anionic surfactant present in a range of 6.0–10.0% (w/w). The other surfactants are the cocoamidopropyl betaine (CAPB), an amphoteric surfactant, also present in both formulations, and one of two non-ionic surfactants alkylpolyglucoside (APG) and cocodiethanolamide (CDEA).

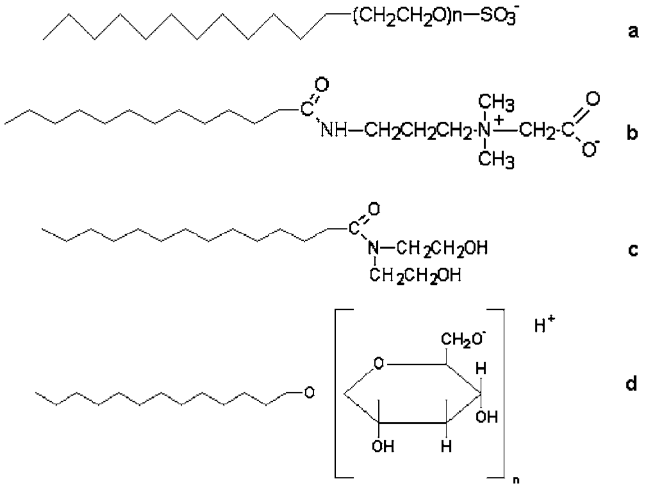

Fig. 1. Structure of (a) sodium lauryl ether sulfate (MW = 384 g mol^{-1}), (b) cocoamidopropyl betaine (MW = 359 g mol^{-1}), (c) cocodiethanolamide (MW = 376 g mol^{-1}) and (d) alkylpolyglucoside (MW = 304 g mol^{-1}).

In the finished formulations, SLES is the only surfactant that can be determined by a direct and fast potentiometric method, using an ion-selective electrode [16,17]. The determination of CAPB, CDEA and APG in finished products presents interference problems that are not well-solved and demand HPLC methods, frequently preceded by laborious solvent extraction [18–22]. By these grounds, even methods for single components at a time in shampoos or liquid soaps are of great interest. As will be shown, application of FTIR-ATR combined with relatively simple chemometrics makes it possible not only to determine one surfactant at a time but all three simultaneously, with the extra bonus of providing also the water content. In this way, time and resources are saved, by overcoming the need of dosing water by the classical Karl Fisher method.

The mid-infrared range absorption spectra of the surfactants considered in this work are presented in Fig. 2. More or less severe superposition of bands is observed, depending on the considered region. The picture is complicated further by the broad and moderately intense absorption bands exhibited by the water molecules, used as solvent. Thus, quantitative determination of the components requires multivariate analysis; the approaches formerly used in infrared analysis range from simple methods like least squares (LS) [23–25] to partial least squares (PLS) for more complicated system responses [26–29].

Although the intended application is relatively complex, it will be shown that it can be handled by straightforward LS methods, without the need of more demanding computations by PLS. Two LS methods of multivariate analysis were compared: the classical least squares (CLS) or Matrix **K** method and the inverse least squares or Matrix **P** (ILS) [30,31]. In both methods, adherence of the absorbance of the analytes to the Beer–Lambert law is assumed. While for CLS

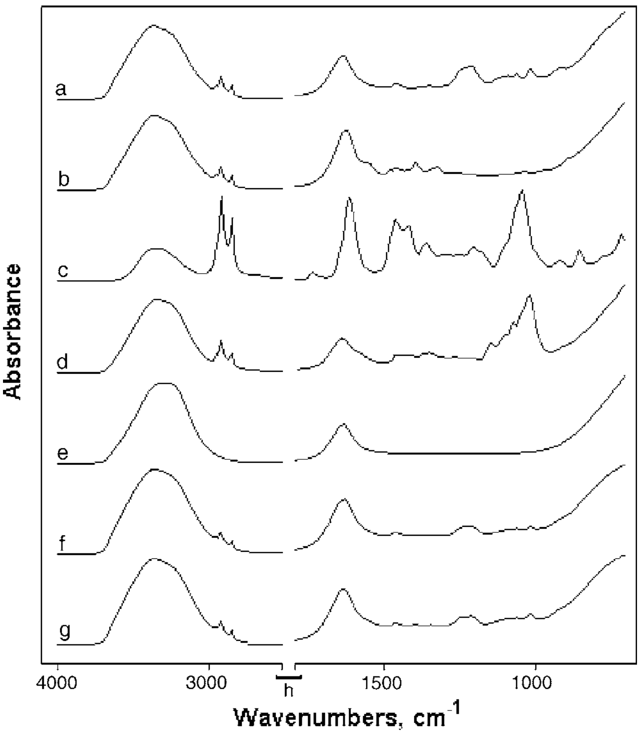

Fig. 2. Infrared spectra of (a) sodium lauryl ether sulfate 27% (w/w), (b) cocoamidopropyl betaine 30% (w/w), (c) cocodiethanolamide 80% (w/w), (d) alkylpolyglucoside 50% (w/w), (e) water, (f) liquid soap, (g) shampoo and (h) blanked region (2515–1800 cm^{-1}).

the absorbance is considered the dependent variable and the calibration coefficients matrix is the absortivity matrix, for ILS the concentration is used as the dependent variable and the matrix calculated has no physical meaning.

- Classical least squares

$$\mathbf{A} = \mathbf{CK} \quad (1)$$

$$\mathbf{K} = (\mathbf{C}^t\mathbf{C})^{-1}(\mathbf{C}^t\mathbf{A}) \quad (2)$$

$$\mathbf{C} = (\mathbf{AK}^t)(\mathbf{KK}^t)^{-1} \quad (3)$$

- Inverse least squares

$$\mathbf{C} = \mathbf{AP} \quad (4)$$

$$\mathbf{P} = (\mathbf{A}^t\mathbf{A})^{-1}(\mathbf{A}^t\mathbf{C}) \quad (5)$$

$$\mathbf{C} = \mathbf{AP} \quad (6)$$

Another difference between the methods is the number of selected wavenumbers for analysis: for CLS, a large number can be handled, possibly helping in noise reduction; the opposite occurs with ILS, where the number of calibration standards sets the upper limit of wavenumbers that can be used. Eqs. (1)–(6) (in matricial notation) summarize the multivariate methods, **A** corresponding to the absorbances matrix (all wavelength and all formulations) and **C** the concentrations of all components in all formulations.

2. Experimental section

2.1. Procedure

The infrared measurements were performed on a Perkin-Elmer Fourier transform spectrophotometer model Spectrum BX with a DTGS detector and a KBr beamsplitter. The ATR accessory was a DuraSamplIR SensiIR with ZnSe/Diamond crystal. The configuration of the cell made possible to perform nine internal reflections.

The spectra consisted of four accumulated scans covering the range from 4000 to 700 cm^{-1} with strong apodization. After acquisition, data in the region of 2515–1800 cm^{-1} was disregarded (blanked), because of interference of the absorption of atmospheric CO_2 and the weak absorption of the diamond on top of the ZnSe window of the ATR accessory, magnified 18 times by the 9 internal reflections, reducing the cell transmission and the energy that achieves the detector. Sample-by-sample intensity fluctuations in the spectra were usually very low and possibly originated by one or more of the following factors: minimum changes in the position of the ATR attachment during the cleaning procedure, variation in the radiation source intensity, fluctuations in the ambient humidity and CO_2 concentration in the region beneath the device. Since utmost repeatability and reproducibility of the spectra are required to reach good accuracy to the multicomponent determination, especially for the most diluted ones, a spectrum normalization procedure was introduced. It consisted in arbitrarily assigning a unity absorbance to the water signal measured at 700 cm^{-1} for all spectra, since the solvent is, by far, the major component of the formulations under consideration. In a refined version, advisable when the water content in the formulation changes widely, the water content of the standards (e.g., as a mass fraction of 1) is used instead as the normalization factor. For the samples, the average water of the standards is used as a starting guess and, once the concentration of all components –including water– is calculated in first approximation, a refinement cycle is applied.

2.2. Reagents and samples

Surfactants used for the preparation of standard and sample solutions were the commercial raw materials used in the mass production of shampoos and liquid soaps, after standardization but without further purification. The analytical methods to assay the surfactant content in each stock solution were classical ones, accepted and widely used in cosmetic companies and chemical industries [16–22]. Water content was determined by the Karl Fischer method. The results of the analysis for the surfactant and water content (in w/w) in the raw products were: 27% SLES (26.42 ± 0.34; 73.60 ± 0.38), 30% CAPB (29.76 ± 0.25; 65.32 ± 0.55), 50% APG (51.96 ± 0.44; 47.85 ± 0.52) and 80% CDEA (80.11 ± 0.63; 0.12 ± 0.01).

Table 1
Levels of the surfactants present in the standard samples

Product	Component[a]	Low level (%, w/w)	Medium level (%, w/w)	High level (%, w/w)
Shampoo	SLES	7.50	8.50	9.50
	CAPB	1.80	2.40	3.00
	CDEA	1.00	1.40	1.80
Liquid soap	SLES	7.80	8.80	9.80
	CAPB	2.20	3.00	3.80
	APG	0.85	1.15	1.45

[a] The water concentration was considered the sum of the water content in each added surfactant plus the added water in the formulation.

Shampoo and liquid soap standard samples were prepared using an analytical balance and a stirrer, mixing all the components of the formulation for 30 min. Of the 45 solutions prepared for each product, 27 were used for calibration purposes (3 levels of concentration for each surfactant, resulting in 3^3 combinations, Table 1), and the other 18, to check the performance of the method (10 random concentrations and 8 more at 2 levels of concentration for each surfactant).

After the spectra acquisition, all data were transferred to a Microsoft Excel worksheet where the least squares calculations were conveniently performed, using pre-programmed matrix operations.

Data treatment by CLS was made with the complete absorbance data set of the selected regions, embracing 200 wavenumbers. For the ILS method, the selection of a reduced set of wavenumbers was favored, as will be discussed.

3. Results and discussion

Spectra recorded under the chosen settings of the spectrometer are presented in Fig. 2 for CDEA and for aqueous solutions of all other surfactants, as well as for water itself. Based on the reference spectra and structural chemical information, Table 2 reproduces the absorption regions found most valuable to discriminate among the surfactants, together with attributions taken from the literature [32–36]. Water was included in the table, because it will be determined too.

Table 2
Absorption regions of the analytes and attributions [32–36]

Component	Region (cm^{-1})	Attribution
SLES	1300–1160	$R{-}O{-}SO_3^-$ asymmetric bend
	1200–950	C—O—C stretch
CAPB	1418–1375	C—N stretch (amide)
	1340–1300	COO^- symmetric carboxylic acid salt
CDEA	1150–1000	C—O stretch
	1650–1500	C═O stretch (amide)
APG	1200–950	C—O—C stretch
Water	3500–3000	O—H stretch
	1700–1550	H—O—H bend

Table 3
Wavenumber regions selected for the CLS method and corresponding surfactant(s) with highest absortivity

Region (cm^{-1})	Components in shampoo	Region (cm^{-1})	Components in liquid soap
1549–1500	CDEA	1472–1423	CAPB
1499–1450	CAPB	1354–1305	CAPB
1349–1300	CAPB, CDEA	1265–1215	SLES
1299–1250	SLES	1162–1113	APG

For the CLS quantification method, data at 200 wavenumbers of the spectrum was used. A comparison was made selecting one contiguous region or selecting four blocks of 50 wavenumbers as given in Table 3. The second procedure was found more satisfactory. For the ILS method, data at the 10 wavenumbers given in Table 4 was used. The wavenumbers were carefully chosen looking for the best compromise of high molar absortivity of the minor components (CAPB and CDEA in shampoo and CAPB and APG in liquid soap) and low relative interference of the other components.

All results obtained for shampoo and liquid soap (Table 5) for both methods, CLS and ILS, are accurate to within 5% or better. Although the regions or the wavenumbers chosen for both calculation methods favor the minor components of the formulations, CAPB and CDEA or APG, the low absortivity of SLES and water at some of these wavenumbers was compensated by their higher concentration. Consequently, even without the inclusion of more selective and intense bands for these major components, they were determined with similar relative uncertainty.

Although the calibration plots of absorbance versus analyte concentration are not exactly linear over the full range, nor do they present null intercepts, by bracketing the relatively narrow concentration range that defines the acceptable limits in the commercial production of such formulations, e.g., as given in Table 1, the linear approximation (required both in the CLS and in the ILS method) was found valid.

Since Table 5 refers to the relative errors, they hide the absolute accuracy (as % of the total mass of the sample) obtained for the minor components. Fig. 3 reveals that they are remarkably low for both formulations and both calculation

Table 4
Wavenumber regions selected for the ILS method and corresponding surfactant(s) with highest absortivity

Wavenumbers (cm^{-1})	Components in shampoo	Wavenumbers (cm^{-1})	Components in liquid soap
2925	All surfactants	2960	All surfactants
1488	CAPB	1488	CAPB
1466	CAPB	1457	CAPB
1430	CDEA	1398	CAPB
1398	CAPB	1327	CAPB
1327	CAPB	1216	SLES
1280	SLES	1152	APG
1083	CDEA	1095	SLES
1044	CDEA	1078	APG
926	CDEA	1030	APG

Table 5
Average, lower and higher relative errors (RE) of the values found by FTIR-ATR for the components in shampoo and liquid soap formulations by both calculation methods

Formulation	Method	Component	Average of modulus of RE (%)	Lower RE (%)	Higher RE (%)
Shampoo	CLS	SLES	0.81	−1.58	1.10
		CAPB	0.94	−2.53	1.11
		CDEA	1.63	−3.17	3.44
		Water	0.32	−0.49	0.76
		Average	0.93	–	–
	ILS	SLES	0.91	−1.73	1.43
		CAPB	1.58	−4.54	2.18
		CDEA	2.42	−5.41	5.47
		Water	0.34	−0.43	0.75
		Average	1.31	–	–
Liquid soap	CLS	SLES	0.61	−1.40	1.05
		CAPB	1.78	−3.05	5.13
		APG	1.66	−4.30	3.70
		Water	0.44	−1.47	0.55
		Average	1.12	–	–
	ILS	SLES	0.69	−1.43	1.23
		CAPB	1.27	−2.21	3.33
		APG	1.51	−3.98	3.81
		Water	0.58	−1.43	0.85
		Average	1.01	–	–

methods. All results are within 0.07% of the expected values, the mean deviations for CDEA being 0.02% by CLS and 0.03% by ILS, and for APG, 0.02% by CLS and 0.02% by ILS. There is also no perceptible change of the random dispersion along the surfactant concentration axis.

The normalization of the absorbance values of all spectra by using water as the "internal standard" is a concept applied here to help to compensate minimum changes or fluctuations in instrumental and environmental conditions and assure higher accuracy. Table 6 reveals that in most cases deviations are slightly reduced after normalization to unity. For the narrow range of water bracketed here, there is no need to refine the normalization by taking into account the water content found in the first calculation (last column of Table 6), although this may be necessary in samples where the "internal standard" can vary in a wider range.

Tables 5 and 6 show that, regardless of using CLS or ILS as calculation method, good results are obtained for all components. CLS was slightly, but not conclusively, better, but may be preferred because its formulation is more conventional and widely accepted. Anyway, there is no need to use the more sophisticated PLS method, adopted by many authors in quantitative analysis by FTIR, as well as NIR. The advantage is that all calculations are fast and can be easily implemented even in a universally available spreadsheet.

As it is, the method can be applied directly in the production process of shampoo and liquid soap, just before the final addition of fragrance. The presence of colorants in such

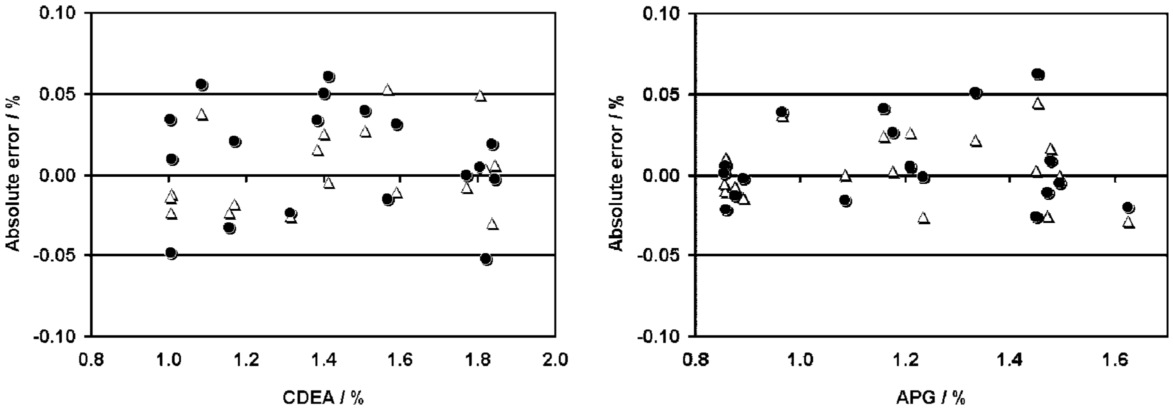

Fig. 3. Comparison of absolute errors resulting from the application of the CLS (△) and ILS (●) methods, for the surfactant in lowest concentration in each formulation, expressed as % of total weight as a function of the actual values. CDEA in shampoo (left) and of APG in liquid soap (right).

Table 6
Average relative error results of the different normalization procedures

Formulation	Method	Component	Average of modulus of relative errors/%		
			Without normalization	Normalized to unity	Normalized to water fraction
Shampoo	CLS	SLES	0.70	0.81	0.85
		CAPB	1.43	0.94	1.02
		CDEA	2.19	1.80	1.86
		Water	0.69	0.32	0.29
		Average	1.25	0.97	1.01
	ILS	SLES	0.91	1.03	1.13
		CAPB	1.70	1.58	1.84
		CDEA	2.43	2.42	2.41
		Water	0.25	0.34	0.31
		Average	1.32	1.34	1.42
Liquid soap	CLS	SLES	0.62	0.62	0.58
		CAPB	2.39	1.78	1.79
		APG	1.71	1.66	1.58
		Water	0.93	0.44	0.39
		Average	1.41	1.13	1.09
	ILS	SLES	0.58	0.68	0.67
		CAPB	1.54	1.28	1.23
		APG	2.08	1.51	1.53
		Water	0.82	0.58	0.54
		Average	1.26	1.01	0.99

formulations is sufficiently low to remain undetected in the spectra, but perfumes may constitute a problem because they can represent up to 1% of total mass, with inevitable spectral interference. Due to the high price of perfumes, their addition is the final step in the industrial production that can be preceded by sample collection for surfactant determination. Analysis of the end product in factory may be considered by subtraction of the fragrance spectrum together with the background, because the dosage of this expensive minor component is relatively constant. For the analysis of products taken from the shelf in a supermarket, the variability of the fragrance concentration with time and from brand to brand represents a problem, which is still under investigation.

4. Concluding remarks

It was shown for the first time that the combination of ATR-FTIR with simple chemometrics like CLS or ILS is very appropriate for the simultaneous analysis of three surfactants and water in shampoo and liquid soap during the production process. Minute amounts of samples, undiluted and without any treatment, are employed; spectra are gathered rapidly and a popular worksheet package suffices for the least squares matrix calculations.

The relative errors for all studied components can be considered similar and possibly better than attainable by conventional analytical methods that are capable of determining a single component at a time, like titrations, potentiometry with ISEs, or extraction followed by chromatography.

If HPLC or capillary electrophoresis methods for the simultaneous determination of this surfactant mixture appear in the future (they are not yet available, to the best knowledge of the authors), disregarding the effluent generation problem of HPLC, in a production plant, they will hardly compete with the combination of additional advantages of speed and ability for concomitant determination of water, although in the case of products taken from the shelf on the market, they may deal better with the variability in the fragrance composition.

References

[1] W.D. Perkins, J. Chem. Ed. 63 (1986) A5.
[2] E. Rosenberg, R. Kellner, Fresen. J. Anal. Chem. 348 (1994) 530.
[3] W.J. Potts, N. Wright, Anal. Chem. 28 (1956) 1255.
[4] E. López-Anreus, S. Garrigues, M. De la Guardia, Analyst 125 (1998) 1247.
[5] F.R. van de Voort, A.A. Ismail, J. Sedman, J. Am. Oil Chem. Soc. 72 (1995) 873.
[6] Y.B.C. Man, G. Setiowaty, J. Am. Oil Chem. Soc. 76 (1999) 243.
[7] J.S. Wong, A.J. Rein, D. Wilks, P. Wilks, Appl. Spectr. 38 (1984) 32.
[8] Z. Bouhsain, S. Garrigues, M. De la Guardia, Analyst 121 (1990) 635.
[9] P.R. Pike, P.A. Sworan, S.E. Cabaniss, Anal. Chim. Acta 280 (1993) 253.
[10] M.L. Ramos, J.F. Tyson, D.J. Curran, Anal. Chim. Acta 364 (1998) 107.

[11] J. Chen, J.A. Gardella, Appl. Spectr. 52 (1998) 361.

[12] M. Gallignani, S. Garrigues, M. De la Guardia, Analyst 119 (1994) 653.

[13] F. Cahn, S. Compton, Appl. Spectr. 42 (1988) 865.

[14] M. Adam, M.M. Massoba, T. Lee, J. Am. Oil Chem. Soc. 77 (2000) 457.

[15] N. Dupuy, M. Meurens, B. Sombret, P. Legrand, J.P. Huvenne, Appl. Spectr. 47 (1993) 452.

[16] M.T. Fielden, P.M. Claesson, J. Colloid Interf. Sci. 198 (1998) 261.

[17] T. Masadome, T. Imato, Fresen. J. Anal. Chem. 363 (1999) 241.

[18] J.M. Platinga, J.J. Donkerbroek, R.J. Mulder, J. Am. Oil Chem. Soc. 70 (1993) 97.

[19] A. Tegeler, W. Ruess, E. Gmahl, J. Chromatogr. 715 (1995) 195.

[20] Y.G. Shin, K.H. Cho, J.M. Moon, M.K. Park, J.H. Park, J. Chromatogr. 857 (1999) 331.

[21] J.J. Hejna, D. Daly, J. Soc. Cosm. Chem. 21 (1970) 107.

[22] M. Castillo, E. Martinez, A. Ginebreda, L. Tirapu, D. Barceló, Analyst 125 (2000) 1733.

[23] B. Gu, J. Wang, Spectr. Lett. 31 (1998) 1053.

[24] J.M. Whittinghill, J. Norton, A. Proctor, J. Am. Oil Chem. Soc. 77 (2000) 37.

[25] X. Otte, R. Lejeune, L. Thunus, Anal. Chim. Acta 355 (1997) 7.

[26] A. Pérez-Ponce, F.J. Rambla, J.M. Garrigues, S. Garrigues, M. De la Gaurdia, Analyst 123 (1998) 1253.

[27] Z. Bouhsain, S. Garrigues, M. De la Guardia, Analyst 121 (1996) 1935.

[28] R. Schindler, B. Lendl, R. Kellner, Anal. Chim. Acta 366 (1998) 35.

[29] S. Garrigues, F.J. Rambla, M. De la Guardia, Fresen. J. Anal. Chem. 362 (1998) 137.

[30] H. Martens, T. Naes, Multivariate Calibration, 1st ed., Wiley, Great Britain, 1989, p. 73.

[31] R.A. Kellner, M. Otto, J.M. Mermet, H.M. Widmer, Analytical Chemistry, Wiley/VCH, Weinhein, Germany, 1998, p. 3.

[32] D.A. Skoog, J.J. Larry, Principles of Instrumental Chemistry, 4th ed., Saunders College Publishing, 1992, p. 252.

[33] G.W. Ewing, Analytical Instrumentation Handbook, 2nd ed., Marcel Dekker, New York, 1997, p. 393.

[34] D.L. Pavia, G.M. Lampman, G.S. Kriz, Introduction to Spectroscopy, 2nd ed., Saunders College Publishing, 1996, p. 14.

[35] D.O. Hummel, Analysis of Surfactants, Hanser/Gardner, Cincinnati, 1996, p. 3.

[36] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, 3rd ed., Academic Press, San Diego, 1990, p. 215.