Mass Spectrometry in the Analysis of non-ionic Detergents

II. Quantitative determination of polyethylenglycole in commercial products

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The amount of PEG contained in several commercial matrices was determined by HPLC coupled with mass spectrometry, using the external standard calibration method. The procedure is rapid and easy enough to apply. It allows as well the detection of ethyleneglycol content in the products containing PEG, if required.

Keywords: non-ionic detergents, liquid chromatography coupled with mass spectrometry, polyethyleneglycole

Commercial polyethoxylated non-ionic detergents are obtained by polycondensation of ethylenoxyde with molecules containing hydrophobic chain, in acidic or basic catalysis and the molecular mass distribution of the product depends on the nature of the catalyst. For a better modulation of the emulsifying properties, it is necessary to control the distribution of molecular masses. In modern technology this requirement is attained by using as catalysts Lewis acids, which creates the premise for a small amount of polyethyleneglycol (PEG) to remain in the non-ionic detergents as an inherent impurity. Due to its lack of emulsifying properties, polyethyleneglycol (PEG) should not be present in significant amounts in non-ionic detergents. Furthermore, the degradation of PEG to hazardous ethyleneglycol has become recently suspected. Consequently, the determination of the quantity of PEG in commercial products has made the object of numerous studies. Non ionic detergents are successfully analyzed by High Performance Liquid Chromatography (HPLC) [1]. Coupling HPLC with mass spectrometry offers valuable information on the structure of the detergents. Protonated molecular ions are obtained as a major result by ionization, together with small amounts of noncovalent adducts with various cations such as lithium, sodium, potassium, silver or ammonium intentionally added in mobile phases [2] The structural analysis of PEG and of several non-ionic detergents was performed by direct injection into the interface generally operated at atmospheric pressure. Various configurations of the mass spectrometer were tested in order to establish the splitting conditions for the molecular ions of PEG. In the end a tandem configuration of the mass spectrometer was used, and the fragmentation was performed by collision with an inert gas [3].

The splitting of the protonated molecular ions of non-ionic polyethylenoxide detergents with one un-functionalized end chain occurs via a charge-induced mechanism, as shown in scheme 1. Obviously, it is not possible to distinguish the particular atom the proton attaches to; however, all resulted fragments have *m/z* values of $44m+1$, were m is the number of the (CH_2-CH_2-O) groups. For non-ionic detergents with at least one free OH group the base peak has a *m/z* value of 133 [3]. For that reason an experiment with multiple reactions monitoring, described as $[M + H]^+ \rightarrow 133$, can be specific both for polyethylenoxide and polyethoxylated non-ionic detergents with at least one free OH group.

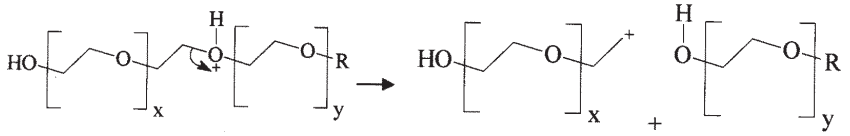
Our previous paper [4] in this series dealt with the analysis of the distribution of molecular weights for derivatizated PEG by HPLC separation and subsequent ultraviolet detection as well as mass spectrometry. In the present article we report the quantitative determination of PEG in various commercial emulsifier matrices such as fatty acids esters or fatty alcoxydes of PEG, using liquid chromatography coupled with mass spectrometry.

Experimental part

Reagents: analytical and chromatographic grade methanol (Fluka), ultrapure water (18.2 MΩ) supplied by a Millipore purification system, commercial 99% polyethylene (PEG) 400 (Fluka).

HPLC has been performed with a Varian system consisting of: Prostar 240 SDM pump, Prostar 410 automatic injector and a triple quadrupol mass spectrometer 1200 L/MS/MS. Chromatographic separation of PEG was carried out with a mobile phase consisting of 90% water and 10% methanol, at a flow rate of 0.6 mL/min, on a Thermo-Hypersil Gold chromatographic column of 50 mm length, 4.6 mm internal diameter and 3 μm particle size. The composition of the mobile phase was isocratic for 15 min , then the column was washed with pure methanol at a flow rate of 1 mL/min and after that follows an equilibration for 10 min. The effluent was divided by a splitter so that 10% was directed to the electrospray (ESI) interface. Air was used as drying gas, at 200°C and a pressure of 20 psi; nebulysing gas was nitrogen, at a pressure of 40 psi. Nebulisation needle has been subjected to a potential of 5 kV, and the source chamber was heated at 50°C.

For the quantitative analyis, a stock solution with known concentration of PEG was prepared, and subsequent dilutions were used for the calibration curve. The two



Scheme 1

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Table 1
CALIBRATION LEVELS OF PEG AND RESPONSE FACTORS

Calibration level	Concentration µg/ml	Response (units)	Response factor
c1	3,46	1.607.000	463.982
c2	6,93	4.055.000	585.391
c3	13,85	8.675.000	626.173
c4	34,64	21.850.000	630.865
c5	69,27	42.590.000	614.840
c6	138,54	86.080.000	621.337
c7	346,35	222.800.000	643.280
	AVERAGE		**597.981**
	Relative standard deviation %		**10,3**

commercial emulsifiers, polyethylenglycol fatty acids esters and polyethoxylated fatty alcohols, were analyzed by repeated injections. All solutions were prepared in methanol and samples of 5 µL of each solution were injected in the chromatographic system. Results were obtained automatically with the MS Workstation software version 6.4.1.

Results and discussions

One of the most complex problems to be solved in the analysis of a commercial mixture arise from the interferences of the matrix components. For example, for the considered detergents, possible interferences are expected between mono- and di-esters or alcoxydes of the polyethyleneglycol, due to the presence of the m/z = 133 fragment, characteristic to both polyethyleneoxide chains with free-OH groups and functionalized polyethylenoxide. The coupling of HPLC with mass spectrometry provides a better solution for these interferences compared to the refraction index detection. In our specific case good resolution is achieved due to significant differences between the retention times of polyethylenoxyde, which elutes faster, and the functionalized products, with longer retention times [5].

The determination of the amount of 400-PEG in the two analysed products was carried out by HPLC using a reversed phase column. The mass spectrometer was set in selected ion monitoring mode for scanning the protonated molecular ions from m/z = 107 to m/z = 635, with increasing values that differ by 44 daltons (i. e. the degree of polycondensation **n** = 3 ÷ 14).

For the quantitative determination, a calibration curve was built, using successive injections of PEG 400 solutions of determined concentrations, namely from 3.46 to 346 µg/mL. The response values obtained are presented in table 1. The response factor is calculated as the ratio between the response given by the detector and the used concentration. The mass spectrometer software automatically draws the calibration curve, taking into account the results of the repeated injections of the calibration standards.

The resultant correlating equation for the calibration curve was:

$$y = 504380x-763397,$$

where x represents the concentration of PEG in the standard solution and y the response signal given by the detector, as the area of the corresponding chromatographic peak.

The dispersion of response values, given by the standard deviation of the response factors, was of 10%. The correlation coefficient r^2 has a value of 0.998, that indicates a good linear correlation between the mass spectrometer response and the PEG concentration of the calibrations solutions. The obtained repeatability for the calibration solutions, corresponding to the fifth level, is of 2%.

Using the calibration curve, a content of only about 1% PEG was determined in both commercial products analysed, value that is consistent with an inherent impurity. The advantage of the above reported method is represented by the fact that it can be easily adapted for the determination of PEG content in other commercial products.

Conclusions

The tandem technique consisting in HPLC coupled with mass spectrometry allows the determination of PEG content in several commercial matrices. The procedure is rapidly and easily applied. The selectivity of the method is ensured by both HPLC separation and selected ion monitoring routine for the mass spectrometer. Additionally, for products that contain PEG, it is possible to determine also the content in ethyleneglycol.

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