

Analysis of Emulsifiers in Complex Matrices

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Introduction

Emulsifiers can be qualitatively and quantitatively analysed in complex formulations of drugs, pesticides or food by a combination of multinuclear NMR spectroscopy and HPLC-MS* analysis.

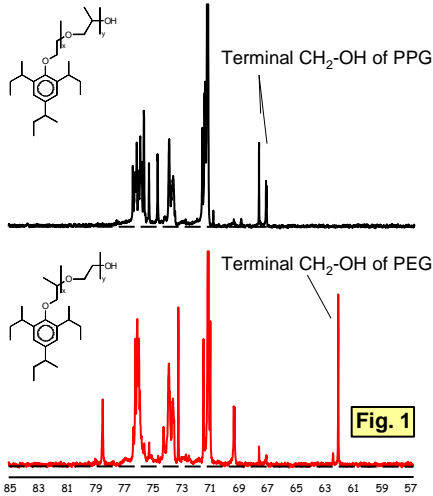


Fig. 1

Sequence Analysis of PEG/PPG Copolymers

The high spectroscopic dispersion of ¹³C-NMR enables the distinction between polypropylene glycol (PPG) and polyethylene glycol (PEG) terminated systems as shown in Fig. 1.

Quantification of Nonylphenol-PEG

Normalisation of the integral areas of the ¹H NMR spectrum enables the calculation of the mean PEG distribution and the alkyl chain lengths (Fig. 2)

$$n = (19.95 + 350)/40 = 9.25$$

The integral value of the alkyl chain between $\delta = 2.0$ and 0.5 confirms the presence of 19 H.

Quantification of Nonylphenol-PEG in complex formulations is possible using the specific integrals (b) or (c) with an internal standard or alternatively by standard addition. Fig. 3 shows the NMR spectra observed by the standard addition of Nonylphenol-PEG in a pesticide before (left and bottom) and after standard addition (right and top)

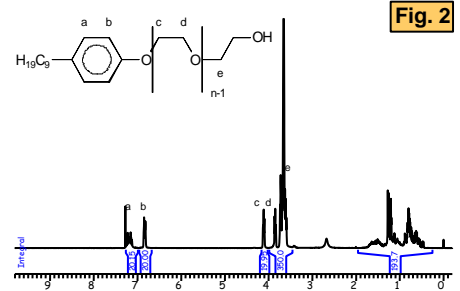


Fig. 2

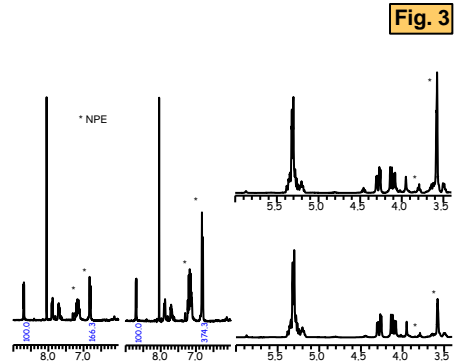


Fig. 3

Fig. 4

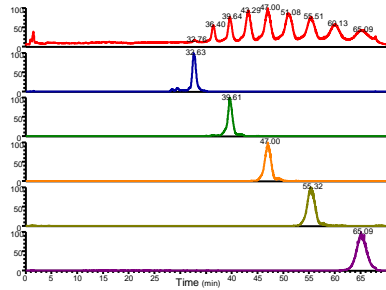
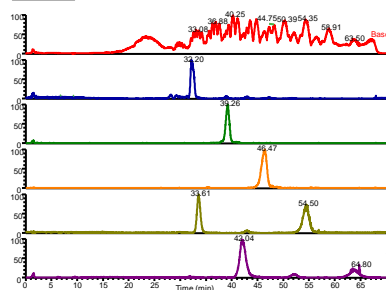


Fig. 5



HPLC/MS of PEG/PPG Copolymers

+ESI mass spectroscopy is very sensitive in detection of polyglycols, -ESI is useful for anionic emulsifier systems.

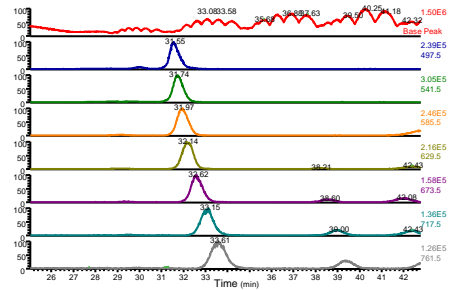
In Fig 4 the HPLC/MS chromatogram of stearyl-PPG-6 is shown. The top trace represents the mass chromatogram (base peak). The traces below correspond to the increasing number of PPG units. The Na⁺ cluster ions are given in Tab. 1.

Fig 5 shows the HPLC/MS chromatogram of a stearyl-PPG-6-PEG-6 copolymer. The top trace re-presents the mass chromatogram (base peak). The traces below correspond to the non reacted stearyl-PPG (PEG = 0)

Tab. 1

RT [min]	M/z	PPG n
32,63	409	2
39,61	467	3
47,00	525	4
55,32	583	5
65,09	641	6

Fig. 6

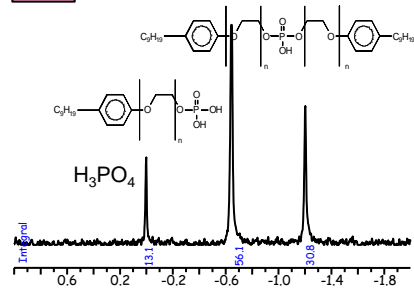


In Fig 6 the HPLC/MS of stearyl-PPG-6-PEG-6 copolymer are separated by traces corresponding to the PEG distribution of a single stearyl-PPG (n = 2) base molecule. The Na⁺ cluster ions are given in Tab. 2.

Tab. 2

RT [min]	M/z	PEG n
31,55	497	2
31,74	541	3
31,97	585	4
32,21	629	5
32,62	673	6
33,15	717	7
33,61	761	8

Fig. 7



³¹P-NMR in quantitative analysis.

Quantification of mono- and diesters of phosphoric acid with modified PEG (e.g. Fosfodet®) and non-reacted phosphoric acid is demonstrated in Fig 7. The molar ratio of all different species can easily be calculated from the integral areas. A suitable internal standard can be used for absolute quantification.

Detection of defined molecules with different PEG chain lengths is possible by changing the pH-value resulting in an optimal spectroscopic dispersion of the monoester signals (Fig. 8).

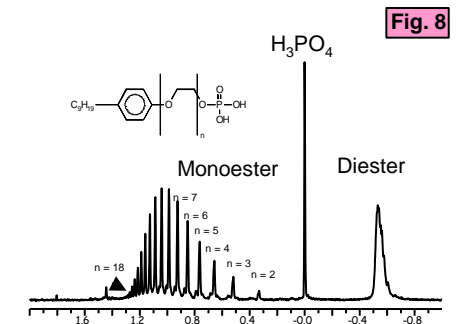


Fig. 8