

Analysis of Nonylphenol Polyethoxylates using GCMS

Nonylphenol is an endocrine disruptor. Nonylphenol is rarely used by itself, but detected as decomposed products from nonylphenol polyethoxylates, a surfactant used in detergents. Typical cases that have been reported are the generation of nonylphenol in sewage and wastewater treatment facilities due to the decomposition of nonylphenol polyethoxylates by enzymes. Lately, nonylphenol polyethoxylates are rarely used in Japan.

This Application News introduces an example of measuring nonylphenol polyethoxylates.

Fig. 1 shows the structural formula of nonylphenol polyethoxylate. The nonyl group, which is a type of alkyl group, generally exists as branched chains, instead of a linear chain. Thus multiple peaks are detected.

Before measurement, the sample was trimethylsilylated by being mixed with a BSTFA reagent and heated at 50 - 60°C for 30 minutes. This reaction is inhibited by water in the sample, so the sample should be completely dehydrated. Table 1 shows the analytical conditions. Fig. 2 and 3 show the mass chromatograms for the typical ion ($M-C_6H_{13}$)⁺ for sample 1 (Co-210: n=1-3) and sample 2 (Co-520: n=0-7). Fig. 4 shows the mass spectrum for n=4. Individual peaks indicate the different isomers, where ion intensity ratio in the mass spectrum differ. Here an average mass spectrum is presented.

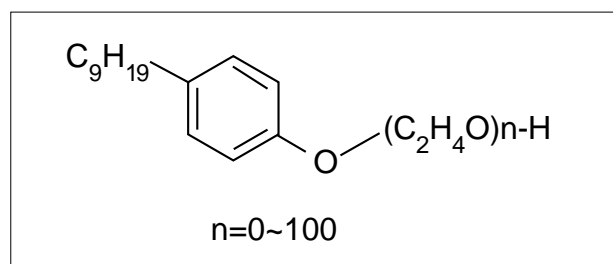


Fig.1 Structure of Polyethoxy nonylphenol

Table 1 Analytical Conditions

Column	: DB-1 30m × 0.25mm I.D. df= 0.25μm
Column Temp.	: 80°C (1min.) - 10°C/min - 330°C (20min)
Carrier Gas	: 250kPa (1min) - 50kPa/min - 100kPa (45min)
Injection Port Temp.	: 340°C
Interface Temp.	: 280°C
Injection Method	: Splitless (Sampling Time : 2min)
Scan Mass Range	: m/z 35-800

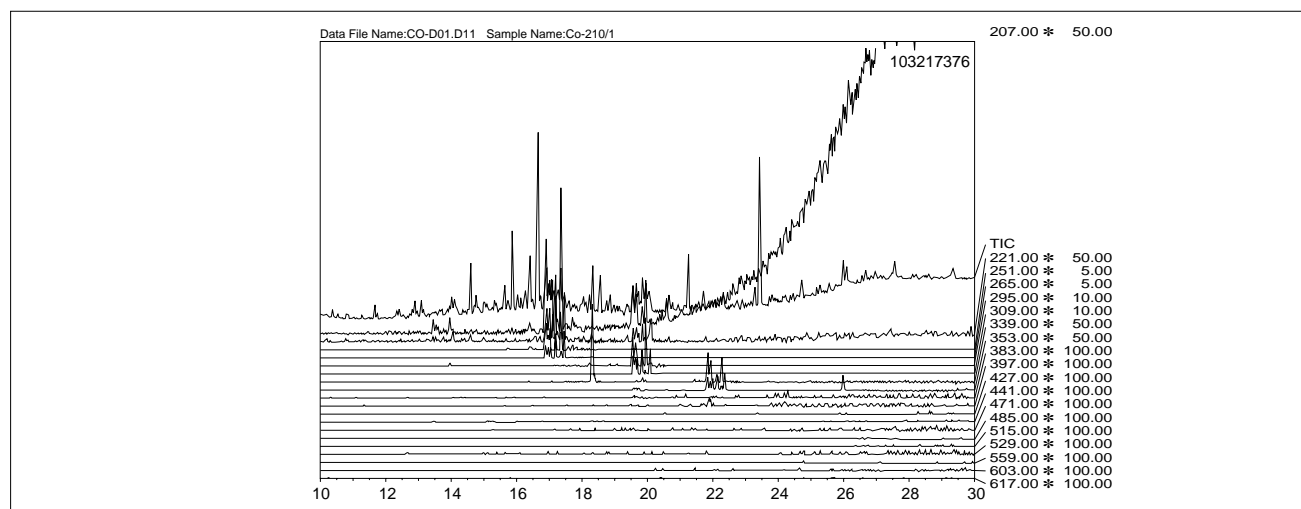


Fig.2 Mass Chromatogram of Nonylphenol Polyethoxylates (n=1-3)

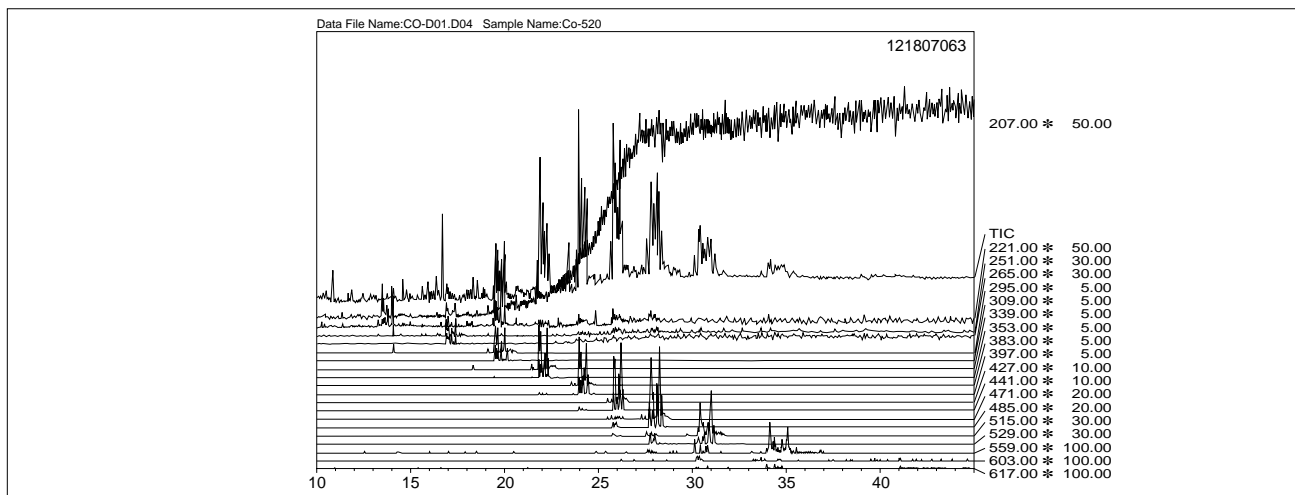


Fig.3 Mass Chromatogram of Nonylphenol Polyethoxylates (n=0-7)

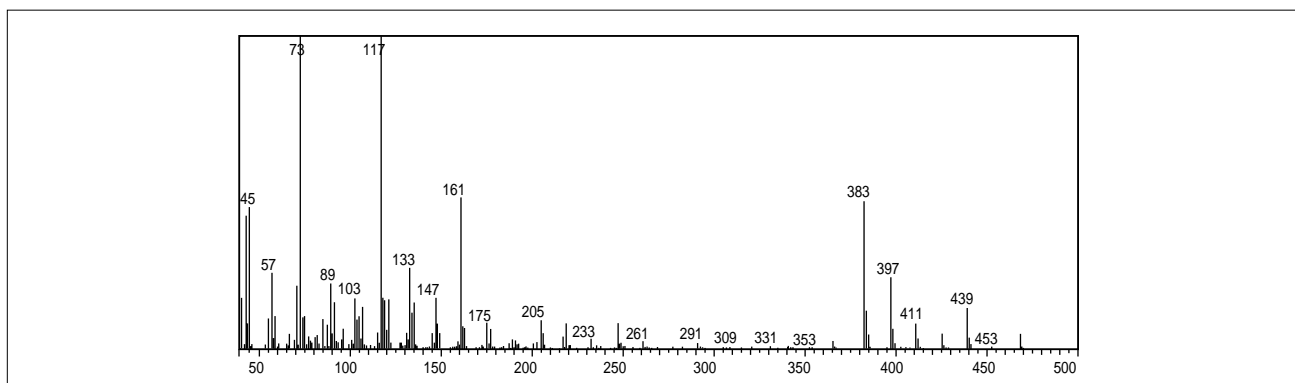


Fig.4 Mass Spectrum of Nonylphenol Polyethoxylate (n=4)

Since nonylphenol polyethoxylates have large molecular weights, GCMS detection is only possible up to $n=7$. So we attempted measurements using a time-of-flight mass spectrometer MALDI-TOFMS, which is capable of measuring compounds with larger

molecular weights. Figs. 5 and 6 show the results for sample 3 (Co-720) and sample 4 (Co-990) respectively. Compounds with high degrees of polymerization are also detected.

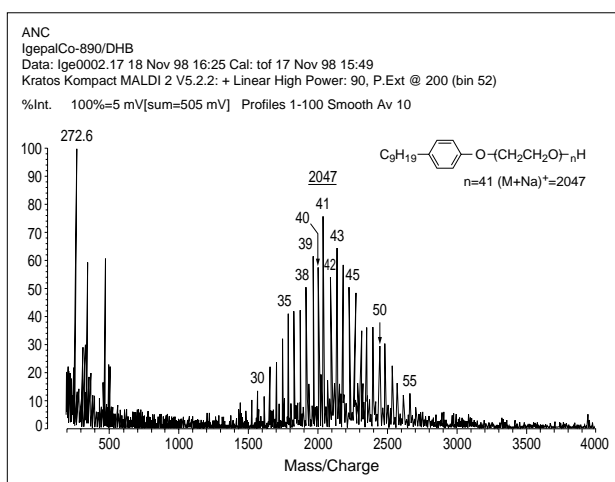


Fig.5 Mass Spectrum (TOF-MS) of Nonylphenol Polyethoxylate

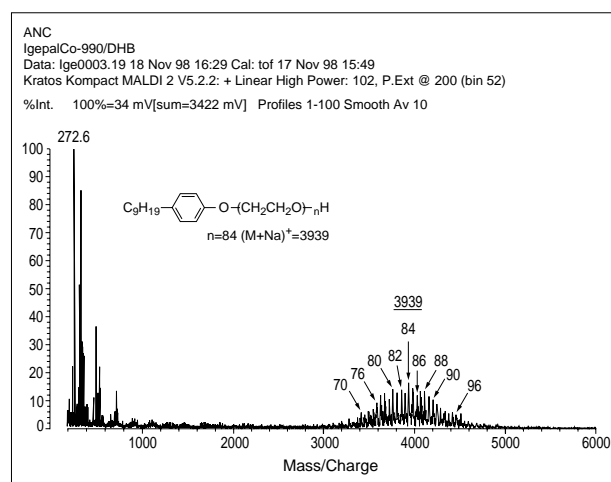


Fig.6 Mass Spectrum (TOF-MS) of Nonylphenol Polyethoxylate

TOFMS can detect up to $n=100$, while GCMS only detects up to $n=7$. Note that standard samples are necessary for accurate quantitation.