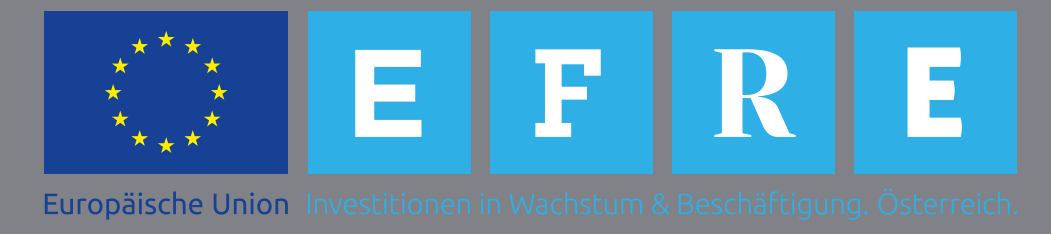
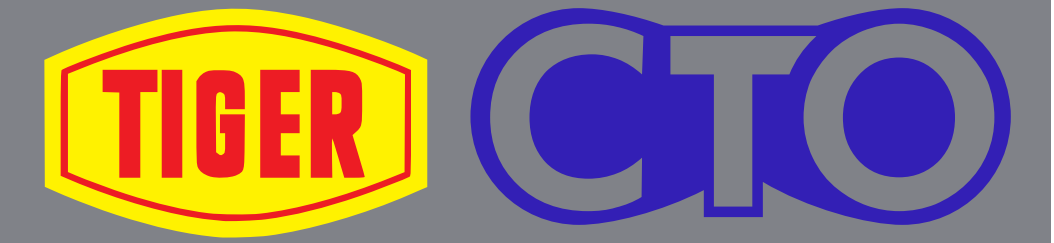


# COMPARISON OF CONVENTIONAL ANALYTICAL AND MASS SPECTROMETRIC METHODS APPLIED ON POLYESTERS

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## Introduction

Due to their versatility, polyesters are popular in different industrial applications such as bottles, fibers, and binders. To understand the influences of molecular structures on crucial properties, several analytical methods are available. Besides conventional methods such as gel permeation chromatography (GPC) and quantification of functional groups via titration (acid value, hydroxyl number), more specific analysis such as MALDI-TOF and direct infusion ESI-Orbitrap mass spectrometry (MS) can be applied.

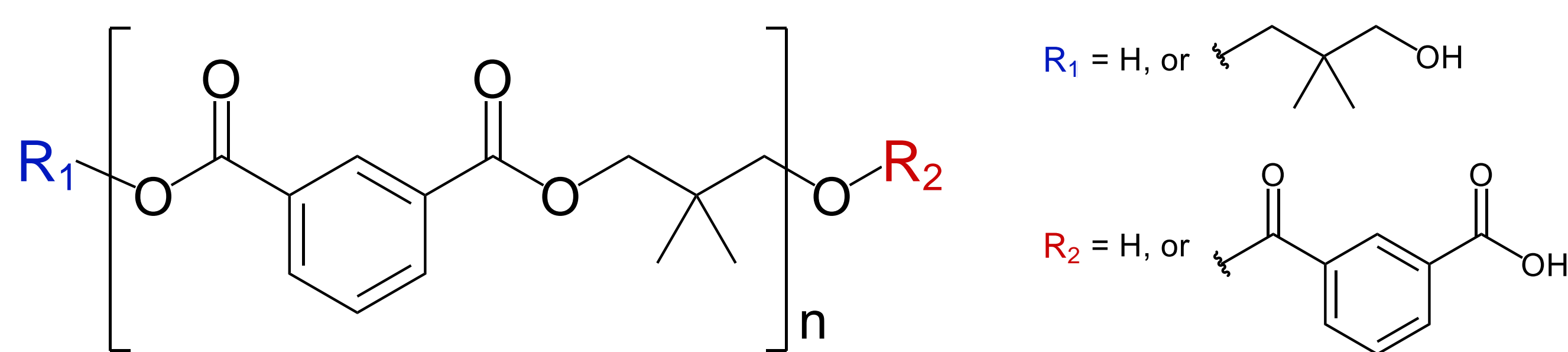


Figure 1: Structure of linear polyesters from isophthalic acid and neopentyl glycol. Excess of one component leads to different functionalization on  $R_1$  and  $R_2$ .

## Experimental and Results

For the comparison of the analytical methods mentioned above, different polyesters (PES) were synthesized using isophthalic acid and neopentyl glycol as monomers (Fig. 1). For carboxyl terminated PES-COOH the acid component was used in excess, PES-OH was synthesized with an excess of neopentyl glycol.

After determination of **acid and hydroxyl value**, the number average molar mass ( $M_n$ ) was calculated and similar results were obtained for PES-COOH (3 620 g mol<sup>-1</sup>) and PES-OH (3 860 g mol<sup>-1</sup>). Calculation of  $M_n$  from **GPC** chromatograms after calibration with polystyrene (PS) standards (Fig. 2) gave significantly lower values of 1 760 and 2 180 g mol<sup>-1</sup>, respectively. It can be assumed that the chosen polyesters have stronger interactions to the GPC column compared to PS and thus, results seem to be distorted.

Fig. 3 shows the mass spectrum of PES-COOH obtained by direct infusion **ESI-Orbitrap MS** (negative mode). Resolution and accuracy were high, but only low masses up to 2 500 could be detected.

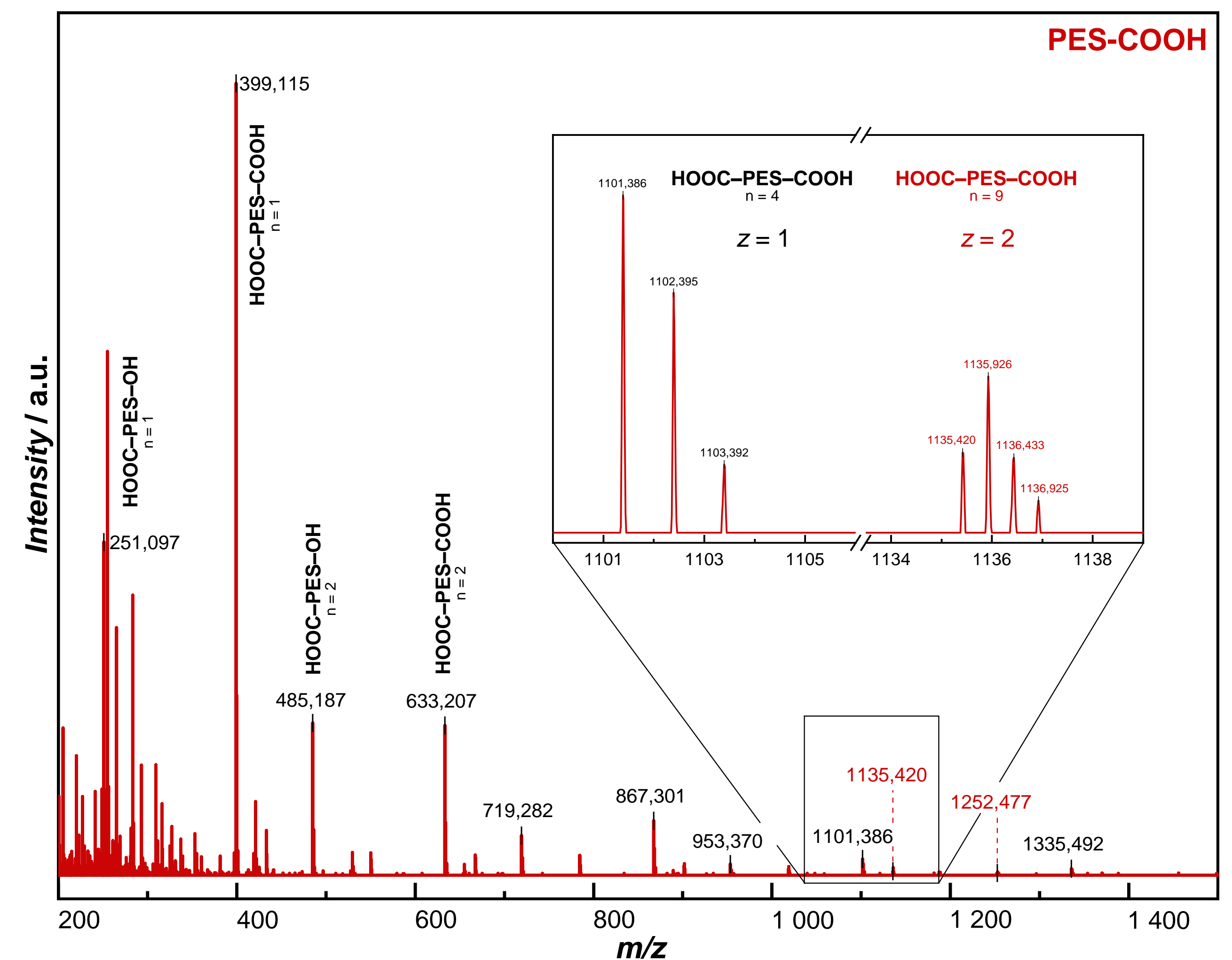


Figure 3: Direct infusion ESI-Orbitrap mass spectrum. High resolution and accuracy was obtained (e.g.  $m/z_{th} = 399,108$  vs.  $m/z_{pr} = 399,115$ ), but only polyesters with  $n \leq 10$  were detected.

**MALDI-TOF mass spectra** are shown in Fig. 4. The regarded  $m/z$  region up to 10 000 revealed similar mass distributions of PES-OH and PES-COOH. Terminating groups could be identified and cyclization products were found. Details are shown in Fig. 5.

However, mass resolution and accuracy were low compared to other polymers analyzed by MALDI-TOF MS. Thus, smaller  $m/z$  regions should be regarded for optimizing the quality of the spectra. This was achieved by fractionating the samples by GPC prior to analysis. For this purpose the eluent was mixed with the matrix solution on-line and directly applied onto the MALDI target via electrospray (Fig. 4).

## Conclusion

Comparing conventional and MS methods for structure elucidation of the chosen polyester system, MALDI-TOF MS seems to provide the most comprehensive information about both molecular mass distribution and functional groups. The combination with GPC fractionation allows optimization of mass resolution and accuracy.

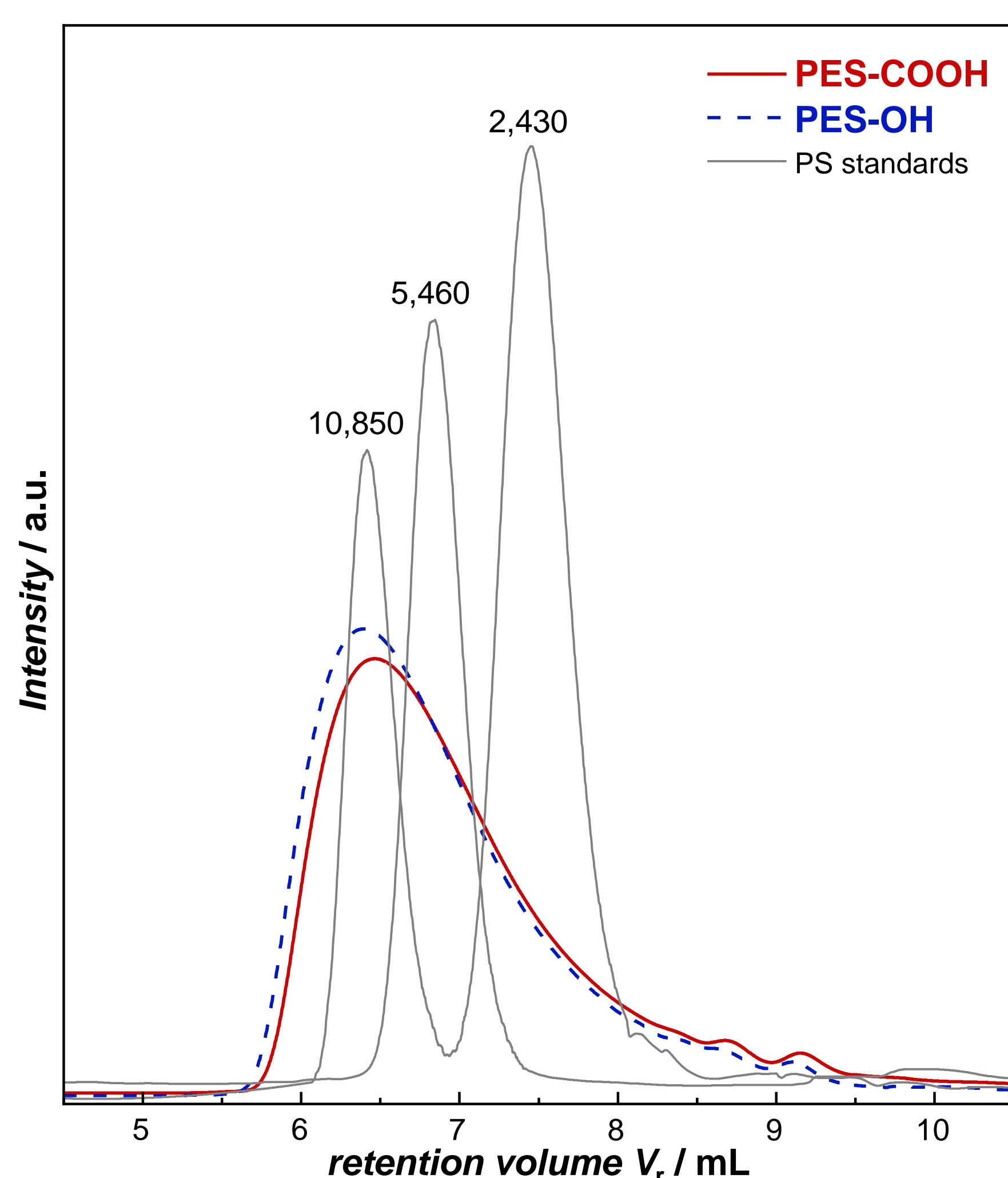


Figure 2: GPC chromatograms. Similar mass distributions are obtained for PES COOH and OH compared to PS standards.

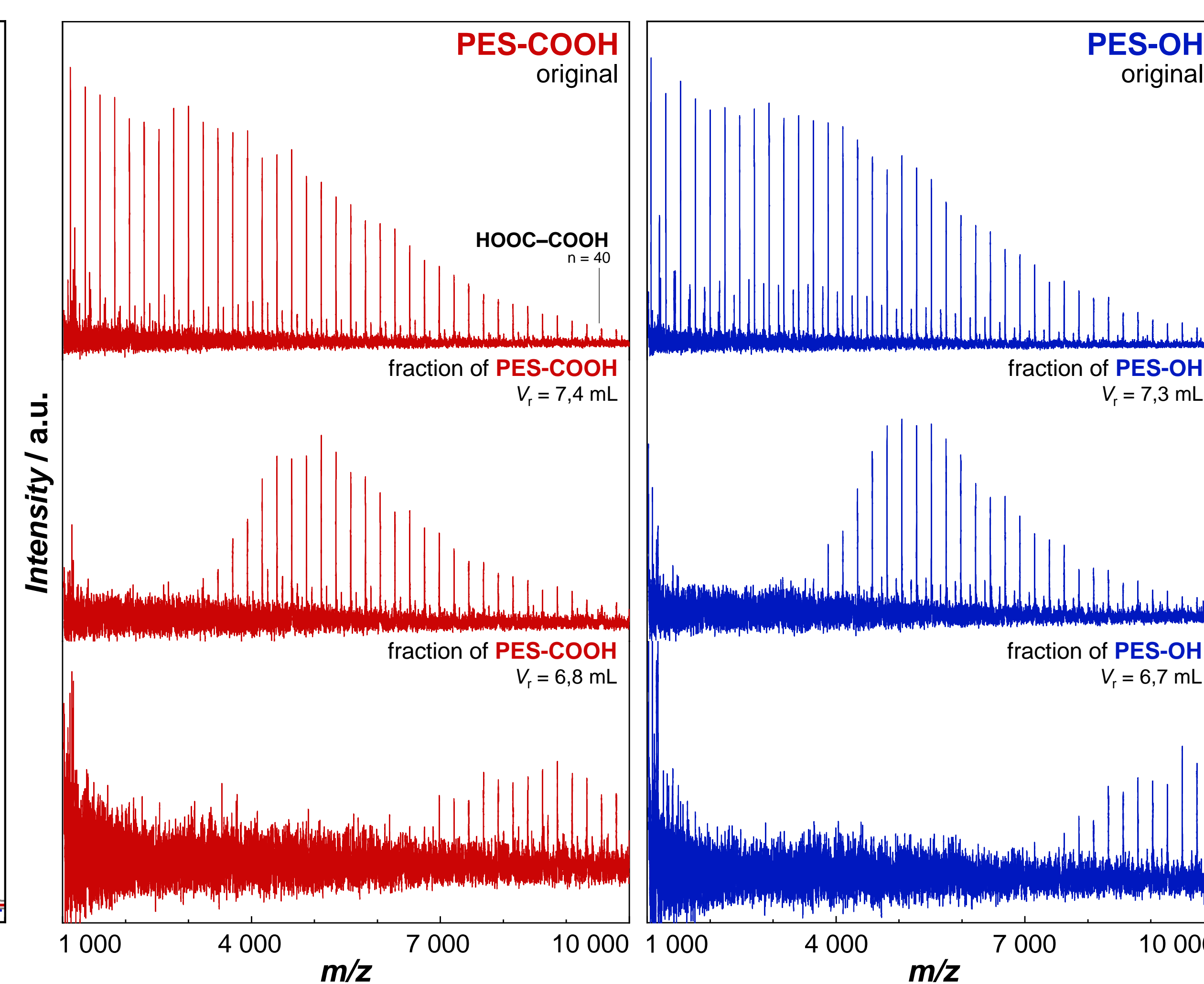


Figure 4: MALDI-TOF mass spectra show similar mass distribution for the polyesters, here up to  $m/z = 10\,000$  (top). To optimize resolution and accuracy, fractionation of polyesters via GPC is necessary and successfully executed by direct application of eluent on MALDI target.

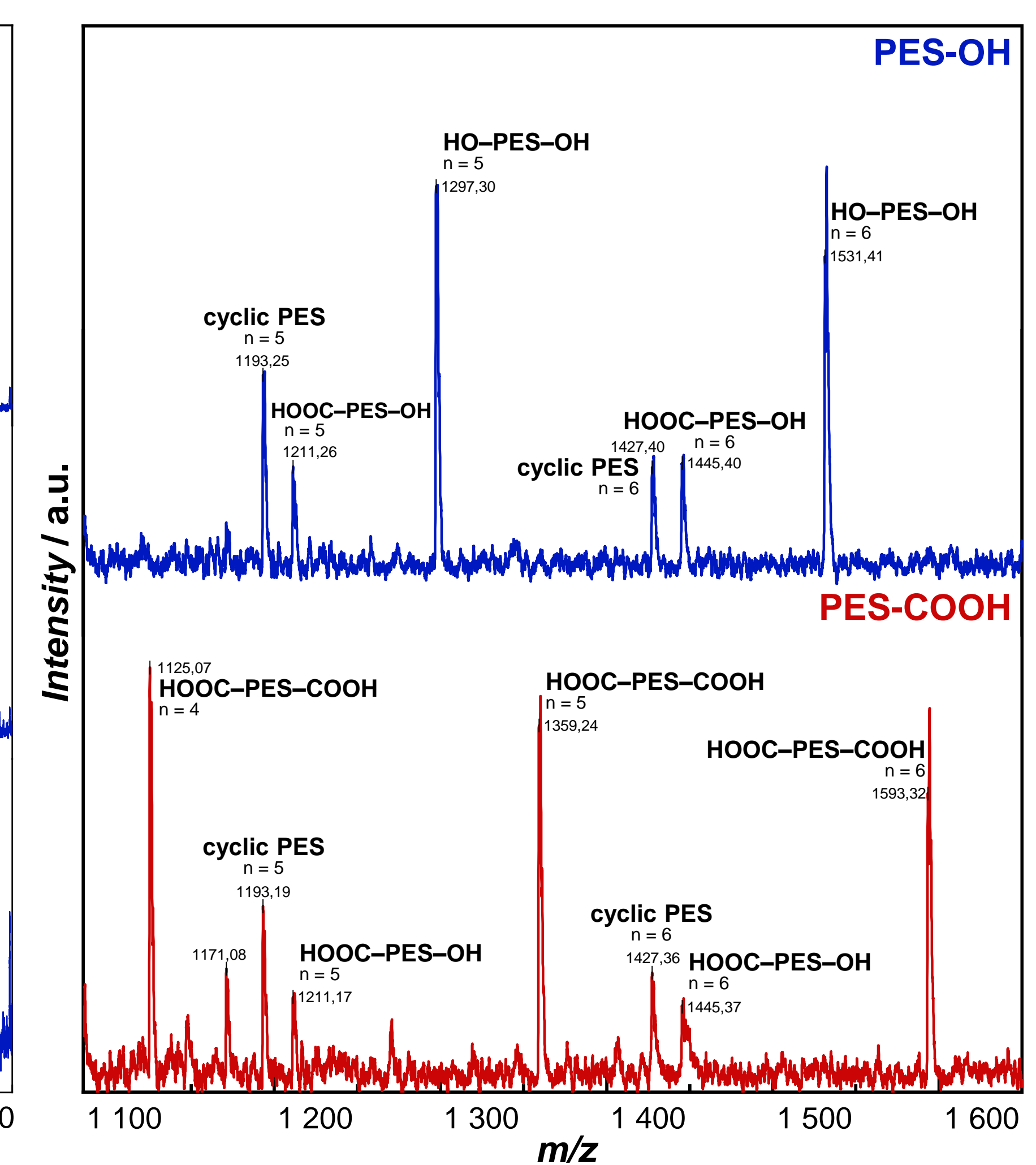


Figure 5: MALDI-TOF MS detail including assignments. For both polyesters terminating groups could be identified and also cyclization was observed.