



Citation for published version:

Rohani, R, Hyland, M & Patterson, DA 2011, 'A refined one-filtration method for aqueous based nanofiltration and ultrafiltration membrane molecular weight cut-off determination using polyethylene glycols', *Journal of Membrane Science*, vol. 382, no. 1-2, pp. 278-290. <https://doi.org/10.1016/j.memsci.2011.08.023>

DOI:

[10.1016/j.memsci.2011.08.023](https://doi.org/10.1016/j.memsci.2011.08.023)

Publication date:

2011

Document Version

Peer reviewed version

[Link to publication](#)

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A Refined One-Filtration Method for Aqueous Based Nanofiltration and UltraFiltration Membrane Molecular Weight Cut-Off Determination using Polyethylene Glycols

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For: Journal of Membrane Science

Abstract

A rapid, reliable and cheap method of characterizing the molecular weight cut-off (MWCO) of commercial and in-house fabricated membranes used in aqueous applications has been developed. MWCO can be determined by performing a single run of pressure filtrations with a mixture of polyethylene glycols (PEGs) in aqueous solution using one of two PEG oligomer mixtures: PEG 200 to PEG 1000 for nanofiltration membranes or PEG 1000 to PEG 6000 for low MWCO ultrafiltration membranes. Analysis is via a repeatable and accurate reverse phase high performance liquid chromatography (HPLC) method through a cheap chemical-bonded silica-based C8 column which finely resolves each of the PEG oligomers. Detection is via a low temperature evaporative light scattering detection (ELSD) method that resolves peaks to a molecular weight difference of just 44 g mol^{-1} (corresponding to the $\text{CH}_2\text{-O-CH}_2$ structural unit difference between the oligomers), allowing the most precise ever one-filtration determination of MWCO. MWCO testing of commercially available membranes (from Koch, Filmtec™ and Hydranautics) confirmed the method gives MWCO in the expected range. Consequently, this new and refined method can effectively replace the previously required time consuming and costly multiple filtrations of individual PEG oligomers and other compounds for the determination of membrane MWCO for aqueous applications.

Keywords: molecular weight cut-off; Polyethylene glycol; HPLC; ELSD detector; C8 column

1. Introduction

The use of pressure driven membrane separations has revolutionised many industries, including the dairy, food and beverage, chemical manufacture and wastewater treatment industries, by allowing the recovery, reuse and/or sale of previously wasted materials. This practice has enabled these industries to become more environmental friendly by decreasing the amount of waste generated, and more cost-effective as more high-value components can be recovered and reused. A number of commercially manufactured and applied membranes have enabled this revolution, with proper selection and application of these membranes being key to further developments in this area. Initial membrane selection for all applications is usually based on the molecular weight cut-off (MWCO) specified by the manufacturer [1]. The evaluation of membrane MWCO, in theory, allows the proper engineering of membrane systems in order to design processes that have predictable performances [2]. There are a number of issues and limitations around the application and use of MWCO [3, 4], however despite these, the measurement and comparison of MWCO and MWCO curves still remains the most convenient and universally applied means of choosing and differentiating between membranes for different applications, prior to evaluating a specific membrane in the actual system of interest. Consequently, a robust, cheap, rapid procedure for the evaluation of MWCO is vital for the current and future membrane industry, the growing application and use of membranes, and the ever growing membrane research area.

A membrane's MWCO is a representation of membrane selectivity for solute molecules of different molecular weights (MWs), where the MW value is obtained from the solute molecule that gives a 90% rejection when a range of different MW solutes are filtered in the target solvent (which for most liquid based, pressure driven membrane applications is water),.

where rejection is defined as in equation 1:

$$\text{Rejection R, \%} = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (1)$$

where C_p and C_f are the concentration of permeate and feed, respectively.

This therefore implies that a membrane rejection study must be performed in order to get a MWCO value. Currently, for ultrafiltration (UF) and nanofiltration (NF) membranes, there is no universally accepted and available, rapid and cheap standard method for doing this. In the methods currently available, a range of compounds with different MWs such as polyethylene glycols (PEGs) [2, 5-8], oligostyrenes [9-11], alkanes [9, 12], dextrans [5, 8, 13-17], pesticides [18] and acids [6] are subjected to one or more pressure filtration tests. Most of these testing procedures are costly, laborious and repetitive, since single compound solutions (with one MW) are tested, requiring four or five separate filtration runs to finally obtain the MWCO curve. This is because there have been few rapid, reliable and relatively inexpensive chromatographic techniques that are able to separate a relatively cheap mixture of the different MW compounds to enable a single filtration test to be used for MWCO determination [2, 17, 19-21]. For those that do exist, there are limitations: for example, the recently developed oligostyrene [9, 10] and PEG methods [21] are for non-aqueous solvents, with the former method requiring the use of relatively expensive reagents and the precision and robustness of the latter not yet robustly and directly proven, in particular by benchmarking against commercially available membranes. This is necessary, since when using a mixture of solutes to characterize UF and NF membranes, pore blocking of bigger molecules on the membrane surface and concentration polarization [2, 13, 22] can potentially selectively hinder the transport of different MW solutes and consequently skew the MWCO value from the actual value. Consequently, a reliable, precise, benchmarked and relatively

inexpensive single filtration method for UF and NF membranes intended for aqueous applications is still required.

A major factor that can invalidate multi-component single filtration membrane tests is the possibility of concentration polarization affecting the membrane filtration and distorting the rejection of the components from the intrinsic rejection and giving an apparent rejection that is specific to the conditions of that particular filtration system only. This is an often used reason for the continued use of single component filtrations to determine MWCO. However, it has been shown that concentration polarization can be minimized or eliminated by using a lower concentration of solutes in the filtration [23]. The concentrations used in the method developed in this work are comparable (and even lower) than other published and increasingly used multi-component MWCO single filtration techniques (e.g. [24]), indicating that the effect of concentration polarization should be minimal.

As stated above, the key to obtaining a reliable, precise, benchmarked and relatively inexpensive single filtration MWCO method is in the analytical methods developed and used to separate the different MW solutes in the feed and permeate and to quantify their concentration. Different techniques have been used and are dependent on the analyzed solutes (e.g. refs [2, 9, 16, 21, 25]) - these are summarized in Fig. 1.

<Fig. 1 here>

The solute MW ranges in Fig. 1 have been divided into two categories: (i) a low range MW from below 10,000 g mol⁻¹, and (ii) high range MW from above 10,000 g mol⁻¹. The higher range MW generally applies to higher MW UF and microfiltration (MF) membranes, whilst the lower range MW is for NF and low MW UF and is the focus of the current work. NF and low UF are of interest since they are used for important membrane separations such as the

removal of pesticides [27], hormones [28] and heavy metals [29], as well as the desalting of dyes in the textile industry [30]. In these MW ranges, the three main molecule types used for MWCO quantification are the oligostyrenes and PEGs for NF and UF, and dextrans for UF only. Dextrans are not commonly used for NF MWCO quantifications, since commercial dextrans are commonly only available with MWs of 1000 g mol⁻¹ and above. PEGs are commonly available from MWs of 200 g mol⁻¹ and lower, so although dextrans have been widely used for UF and MF [5, 8, 13-17], they are not suitable for the NF MWCO range considered in this work. Compared to oligostyrenes, PEGs are also more suitable for MWCO characterisations, since they are cheap and available in bulk, making them favourable for repeated separation testing by those on a restricted budget. PEGs in particular have received great attention due to their wide range of MWs, which are suitable for the separation studies of many types of membranes, in contrast to n-alkanes where only MWs below 600 g mol⁻¹ can be well resolved [12, 31]. PEGs also have low membrane solute interaction resulting in insignificant irreversible solute adsorption on the membrane surface [2]. PEGs are therefore ideal for a simple and reliable method to characterize the MWCO of NF and low UF membranes and therefore mixtures of PEG oligomers are the focus of the current work.

A number of different chromatographic techniques have been specifically targeted for separating and quantifying PEG oligomers in the NF and low UF MW range (Fig. 1). The separation and detection of a mixture of PEG oligomers is difficult, as methods usually suffer from a non-linear baseline and/or poor peak resolution. For chromatographic methods, resolution is particularly poor for PEGs with a MW over a few hundred Daltons (g mol⁻¹) [32-34]. Excellent reviews of PEG HPLC and chromatographic separations can be found in refs [7, 15, 20, 34, 35]. Consequently, only a selection of these papers will be outlined here, for the sole purpose of establishing the important past precedents that the current work builds upon.

Successful PEG separations have been achieved with the more expensive techniques of size exclusion chromatography (more specifically gel permeation chromatography, GPC) [2], higher temperature (80°C) multi-column reverse phase high performance liquid chromatography (HPLC) and supercritical fluid chromatography [7], capillary gel electrophoresis [36], liquid chromatography coupled with mass spectroscopy (LC-MS) [34] and ion exchange chromatography [37]. There are many disadvantages with these methods however. For example, GPC requires a special, relatively expensive column for the separation of PEG, since the PEG is known to stick to the more common GPC column stationary phases in order to avoid column contamination. For instance, the use of GPC for the detection of PEG 300 in non-polar long chain free fatty acids resulted in overlapping PEG and acid peaks, necessitating the use of further detection techniques [32] and therefore further time and expense. GPC is also unable to accurately resolve PEG oligomers below a MW of 300 g mol⁻¹ [21]. The use of supercritical fluid chromatography coupled with a flame ionization detection enabled the separation of a mixture of PEG oligomers with MWs ranging from a few hundred to several thousands of Daltons. This technique however gave chromatograms with poor baselines and peak resolution [7]. Capillary gel electrophoresis allows the separation and quantification of PEGs with MWs up to thousands of Daltons, but requires time-consuming sample preparation by derivatization [36] making this method less attractive for large scale analysis compared to the other methods. Ion exchange chromatography has been used in the separation of PEG derivatives [37], however the preparation and refining of the method is relatively complicated since PEGs are non-polar and have non-ionized sites. Consequently, an ionic compound must be added to the mobile phase to produce good retention and peak resolution. Finally, LC-MS has been tested and has been found to give reasonable peak resolution [34], however the high purchase and maintenance cost of LC-MS equipment is a significant barrier to the wide adoption of this technique. The most promising

technique for PEG separation and quantification has been HPLC coupled with evaporative light scattering detection (ELSD), which allows the determination of individual PEG oligomer concentrations [33, 38]. As previously mentioned, this technique has also been proposed (but not yet robustly proven) for the characterization of the MWCO of organic solvent resistant NF membranes [21], but has not yet been robustly demonstrated. A new MWCO testing method is therefore required to overcome these problems, in particular for membranes applied in aqueous applications (i.e. the majority of membranes and their applications). This research therefore aims to develop a cheap, low temperature, robust, benchmarked single filtration method for determining the MWCO of NF membranes for aqueous based separations using a mixture of commercial grade (i.e. off-the-shelf) PEGs, which contain a wide range of different MW PEG oligomers. This will be benchmarked against the MWCO and membrane separation properties of commercially available membranes using data provided by both the manufacturer and from previous characterisations in the open literature. Note that the membranes of interest also separate salts by the Donnan Effect, so the MWCO method outlined in this paper is not intended as a replacement for the characterization of salt rejection on such membranes, but rather an accompanying test that can be easily run in parallel to characterize the organic molecule type MWCO (effectively organic rejection characteristics) for these membranes.

2. Methods and Materials

2.1 Materials

NF membranes were kindly donated by the Dow Chemical Company (Dow Filmtec™ membranes), USA and were purchased from Koch Membrane Systems, USA and

Hydranautics, USA. Their characteristics and properties are summarised in Table 1. Commercial grade PEGs were obtained from several different companies, as detailed in Table 2. Additional PEG standards were used for external calibration (Fluka, Product no 87976) as detailed in Table 2. HPLC grade Acetonitrile (Ajax Finechem, New Zealand) was used for all HPLC analysis. All chemicals were used as received. Deionized water from an ELGA Maxima Ultra purifier system was used throughout.

<Table 1 here>

<Table 2 here>

The MWCO PEG mixtures were diluted in the deionised water to produce PEG oligomer mixtures with two ranges of MW: (i) NF MWCO range: 200, 400, 600 and 1000 g mol⁻¹ and (ii) low UF MWCO range: 1000, 1500, 4000 and 6000 g mol⁻¹. Two PEG oligomer ranges needed to be used since it was not possible to develop a single HPLC-ELSD method that could separate all of these PEG oligomers in a reasonable elution time (less than 60 min) with good peak resolution. For external calibrations (to get concentration versus area calibration curves for all of the component PEG oligomers), in order to ensure that the peak response from the ELSD detector was similar for all oligomers within these ranges, two different concentrations of the commercial grade PEGs were used: 50 to 400 mg L⁻¹ for PEG 200 to PEG 1500, and 25 to 200 mg L⁻¹ for PEG 4000 to PEG 6000. Getting a relatively uniform peak response for the different PEG ranges used is important so that the peaks do not overlap and are well resolved. The peaks obtained from the PEG 4000 and PEG 6000 powders have a much larger detected response than the lower MW PEG oligomers, therefore the concentrations needed to be lower to ensure peak areas and heights were comparable across the entire HPLC chromatogram.

2.2 Analytical Methods

An Agilent 1100 Autosampler HPLC system coupled with an Alltech[®] ELSD 800 detector was used. The Agilent 1100/1200 series system consisted of: an ALS 1200 series autosampler (G1329A), a Colcom column oven (G1316A), a Quat pump (G1311A), a degasser (G1379A), a UV-Vis detector (G1314A) (not used in this work) and an Agilent data interface (35900). The separation was achieved using an Alltech Altima C8 column (150 mm length x 4.6 mm I.D., 5 μ m particle size, 80 Å pore size) from Grace Davison Discovery Science (New Zealand). The autoinjector was set to one injection per sample with an injection volume of 50 μ L used for all samples. The column temperature was set at 50°C and the ELSD drift temperature at 60°C under a nitrogen pressure of 43 psi (2.9 bar). The mobile phase was pumped at 1.0 mL min⁻¹. HPLC method development resulted in two different acetonitrile-water mobile phase gradients in order to resolve the individual peaks from the low and high MW PEG mixtures respectively as presented in Table 3. Post run, for both gradient profiles, the solvent was left to run at the original acetonitrile-water ratio for 5 min in order to re-equilibrate the column and to ensure a linear baseline for the next run.

<Table 3 here>

Commercial PEG mixtures contain a range of PEG oligomers as do the different PEG standards that can be used for identification and external calibration, which means that a combination of several different methods are required to accurately determine the MW of the individual oligomers. Therefore two different sets of PEGs were used for individual PEG oligomer identification:

- (1) The commercial grade PEGs that were used in the overall MWCO PEG mixtures in both the NF MWCO range (PEG 200 to PEG 1000) and the UF MWCO range (PEG 1000 to PEG 6000). The same HPLC-ELSD method was used, except the individual concentrations of the PEG prepared were increased to five times higher than the MWCO PEG mixtures with double the HPLC injection volume in order to have a comparable peak sizes to the PEG oligomers in the MWCO PEG mixtures.
- (2) The aforementioned purer PEG standards (Section 2.1), used as received and using the same HPLC-ELSD method outlined above.

Note that mass spectroscopy detection was not used for oligomer identification, since PEGs are notorious for contaminating these detectors and a different HPLC gradient method that is compatible with the requirements of the mass spectroscopy detector would be required.

2.3 Filtration Method

PEG MWCO mixtures at a concentration of 400 mg L⁻¹ were permeated through commercially available composite polymeric NF membranes using a water bath temperature controlled dead-end filtration cell (HP 4750, Sterlitech Corporation, USA; active membrane area, 14.6 cm²) as illustrated in Fig. 2. During filtration, the water bath temperature was maintained at 25°C, the dead-end cell was stirred at 300 rpm using a Heidolph MR3004 Safety magnetic heater stirrer and the applied pressure was 30 bar nitrogen gas (BOC, New Zealand). All membranes were preconditioned by filtering with deionised water at the applied pressure until a steady state flux was guaranteed. After reaching steady state, 100mL of the PEG mixture was put into the filtration cell and 40mL of permeate was collected. Permeate volume versus time was recorded to determine the membrane flux. At the end of the filtration, the feed, permeate and retentate were collected and the concentration was analyzed

using the HPLC-ELSD as detailed in Section 2.2.

<Fig. 2 here>

Solute rejection (R) was calculated using equation 1. The membrane flux (J) is defined as the volume of solvents that passes through the unit area of the membrane per unit time, and was calculated using equation 2:

$$J = \frac{\Delta V}{A\Delta t} \quad (2)$$

where V is the volume of permeate, A is the membrane active area and t is the filtration time.

MWCO curves were constructed by plotting the rejection of the individual oligomers in the PEG mixtures against their molecular weight, with the membrane's MWCO determined as the MW that has a rejection of 90%.

3. Results and Discussion

3.1 HPLC-ELSD Characterisation of the MWCO PEG mixtures

In most PEG HPLC separation studies reported previously using ELSD [32, 33, 39], high resolution peaks could only be obtained for PEG oligomers with MWs below 600 g mol⁻¹. Fig. 3 shows that the gradient reverse phase C8 separation coupled with the Alltech® ELSD 800 developed separates both the NF and low UF MWCO range PEG mixtures giving highly resolved PEG oligomer peaks from PEG 200 to PEG 1000 (NF mixture) and from PEG1000 to PEG 1500 (low UF mixture) respectively with stable, straight baselines enabling precise and accurate peak area quantification at a range of concentrations (200, 400 and 800 mg L⁻¹). PEG 4000 and PEG 6000 (in the low UF mixture) could not be separated in a reasonable

elution time. In studies using other detection methods (such as refractive index and low wavelength UV-Vis) coupled with reverse phase HPLC [2, 34, 40], stable baselines were difficult to achieve, since these types of detectors experience baseline drift when mobile phase gradients are employed. Furthermore, the method presented in this work has a straighter, more stable baseline than that in other PEG reverse phase ELSD HPLC methods, such as that in ref. [21]. The HPLC-ELSD method presented here is therefore a significant improvement on past methods.

Note that unlike other PEG separation and quantification methods (such as size exclusion chromatography and GPC), a direct quantitative relationship cannot be determined between MW and retention time. This is because the reverse phase silica based C8 column separation mechanism is based on the competition between the selective adsorption of the chemically bonded phases of the column and the solubility of the oligomers in the mobile phase. The retention time still loosely relates to the MW of the PEG: the higher the MW of PEG, the longer the non-polar chain and the more non-polar the PEG oligomer becomes – thus prolonging the retention time (Table 4). Therefore the lower MW PEG oligomers elute first (have a lower retention time) and higher retention times for higher MW PEG oligomers. The high resolution of the developed method allows a huge MW range of oligomers to be used to determine MWCO, the MW difference limited only by the CH₂-O-CH₂ structural unit difference between them (Table 4).

<Fig. 3 here>

<Table 4 here>

Note that the temperature used to get a successful detection in ELSD (at 60°C) is much lower than previous work, especially for the higher molecular weight of PEG and/or the mixture of PEG compounds, providing an energy saving if this method is adopted. Previous

methods typically used temperatures to evaporate the solution in ELSD were typically above 90°C (depending on the types of mobile phase used). For example, in the case of water and tetrahydrofuran (THF), 90°C was used to detect and quantify PEG 300 in vegetable oils [32]. Other work used a higher temperature (104°C) for detecting the PEG in methanol or acetonitrile [33]. A higher temperature of 95°C has also been reported for detection of PEG in methanol [21]. In previous research, when lower temperatures were used in the ELSD for separation of PEG with MWs above 600 g mol⁻¹ [38], peak separation and baseline stability became poor.

Overall, Fig. 3 shows that the peaks are finely resolved enough that individual PEG concentrations can be easily quantified for MWCO determination. Table 4 shows that there is not a direct correlation between the average molecular weight of the commercial PEG mixture and the actual molecular weight of the main component oligomers. This is because (as mentioned previously) commercial PEG mixtures contain a range of PEG oligomers, as do the PEG standards that can be used for identification and external calibration. Consequently, a combination of several different methods were used to accurately identify the MW of the individual oligomers corresponding to the different peaks in the HPLC chromatograms of the NF and low UF PEG mixtures.

3.2 Determination verification and calibration of the MW of each of the resolved oligomeric peaks

As outlined in Section 2.2, to ensure the MW of each of the peaks in the NF and UF mixtures were robustly identified and verified, two different sets of PEGs were used as external standards:

3.2.1 PEG External Standards and Identifications 1: Commercial grade PEGs

When each of the commercial PEGs is separated using the developed HPLC-ELSD method (Fig. 4), it is apparent that the commercial PEGs contain a number of different unidentified peaks. From these one peak can be rigorously identified– this is the peak corresponding to the average MW (M_n) as shown in Table 2. This was identified as follows: each of the commercial grade PEG yields a well resolved normal (Gaussian) distribution chromatogram of the PEG oligomers from the HPLC-ELSD method developed, with one major peak at the centre, which is the M_n , as shown in Fig. 4. Therefore the retention time of the M_n oligomers can be identified.

<Fig. 4 here>

Note that this still does not give a robust identification of the MW of these peaks, since there are no pure PEG oligomers with a MW of 200 and 400 g mol⁻¹. This method therefore does not give a direct identification, but rather narrows down the identity of the peaks to those close to that MW. Added to this is the fact that the M_n for commercial grade PEG 600 and 1000 given by the manufacturer is a range anyway (Table 5). So the identified M_n peaks have a range of possible ‘true’ identities (Table 4), which are:

- $M_n = 200 \text{ g mol}^{-1}$, closest PEG MW = 194 or 238 g mol⁻¹
- $M_n = 400 \text{ g mol}^{-1}$, closest PEG MW = 370 or 414 g mol⁻¹
- $M_n = 570\text{-}630 \text{ g mol}^{-1}$, closest PEG MW = 546, 590, 634 or 678 g mol⁻¹
- $M_n = 950\text{-}1050 \text{ g mol}^{-1}$, closest PEG MW = 898, 942, 986, 1030 or 1074 g mol⁻¹

The M_n peaks can however be directly identified within the NF (Fig. 4i) and low UF (Fig. 4ii) MWCO chromatograms through matching peak retention times, since the peaks

from the each commercial grade PEGs chromatograms are approximately the same as those in the NF and low NF mixture's chromatograms. (There is some slight shifting of the retention times, albeit in an easily accountable way. This is due to a different oligomeric concentration distribution in the individual PEG mixtures compared to the MWCO NF and UF mix, which resulted in some of the peaks having a higher intensity than in the NF PEG mixture, thus shifting the retention times slightly). The retention times attributable to peaks identified in this way are summarized in Table 5.

<Table 5 here>

Since the peaks cannot be precisely identified from the commercial grade PEGs, purer external PEG standards were also used to further narrow down the identifications above.

3.2.2 PEG External Standards and Identifications 2: Purer PEG standards

The purer PEG standard solutions were analysed in the same way (Fig. 5). Despite only producing a single peak in GPC-SEC (data supplied by the manufacturer), using the HPLC-ELSD method developed in this work, these PEG standards were separated into a range of PEG oligomers like the commercial grade PEGs, albeit with fewer oligomeric peaks, thereby allowing more confidence in assigning MW. This shows that the HPLC-ELSD method in this work produces results more precisely representative of the PEG oligomer purity and distribution than the GPC-SEC method used by the PEG standards manufacturer.

<Fig. 5 here>

Using Fig. 5, the highest peak (M_p) value of the PEG standard (as given by the manufacturer) was attributed to the centre (highest response) peak in the distribution. M_p is a measured average MW, so may vary from a pure PEG oligomer MW due to non-idealities, such as if

the PEG analysed has bound water or had some branched chain content. Like before, the MW attributed to the peak is therefore matched to the nearest MWs of a pure PEG oligomer (as in Table 4). Therefore the following attributions were made (based on Table 4):

- $M_p = 232 \text{ g mol}^{-1}$, closest PEG MW = 194 or 238 g mol^{-1}
- $M_p = 329 \text{ g mol}^{-1}$, closest PEG MW = 326 or 370 g mol^{-1}
- $M_p = 628 \text{ g mol}^{-1}$, closest PEG MW = 590 or 634 g mol^{-1}
- $M_p = 982 \text{ g mol}^{-1}$, closest PEG MW = 942 or 986 g mol^{-1}

Through matching peak retention times, as before, these PEG oligomers of the purer PEG standards were also identified in the NF PEG MWCO mixture chromatograms (giving the MW peak retention time attributions summarised in Table 5, row 2).

3.2.3 The combined oligomer peak MW attribution

Peak identification was then finalized by comparing the narrowed down identities of the various oligomer peaks from the two different PEG standards above and reconciling the MW differences that should exist between all of the peaks in both the NF and low UF chromatograms through the fact that the PEG oligomers differ by one ethylene glycol monomer of MW 44 g mol^{-1} (Table 4). This ensured that the spread of MWs between the identified oligomers matched to the expected differences in structures. From this, the peaks and retention times could only be matched to the MW of each of the expected oligomers (as in Table 4) one way, as shown in Fig. 6 and Table 5 (rows 3 for the NF PEG mixtures and row 5 for the low UF PEG mixtures).

As a result, for the NF range from Fig. 6(i), using the commercial grade PEGs from PEG 200 to PEG 1000, all of the MWs of the separated oligomers were rigorously identified and range from 106 to 1250 g mol^{-1} and for the low UF range, from Fig. 6(ii)), using commercial

grade PEGs from PEG 1000 to PEG 6000, the MWs of the separated oligomers were also all identified and range from 634 to 1646 g mol⁻¹, with unseparated peaks corresponding to MWs of 4000 and 6000 g mol⁻¹.

<Fig. 6 here>

Fig. 6 therefore forms the basis of identifying the MW for MWCO analysis for membranes with a MWCO in the NF and low UF range, since the MW of the PEG oligomers that are permeated and retained by a membrane can be easily identified.

3.2.4 Obtaining linear calibrations and calculating a MWCO curve

In order to use this fully MW specified chromatogram to construct a MWCO curve a plot of rejection of the PEG oligomers versus the MW of these oligomers needs to be determined. Rejection can be calculated from equation 1, so long as each of the peak areas for each of the oligomers can be converted into a concentration, by running (and keeping up-to-date) a set of external calibration curves for all of these oligomers. This must be done for the chromatograms from the NF and low UF PEG mixtures (and not the individual commercial grade PEGs), since the peak response in the ELSD changes between the individual commercial grade PEGs and when they are all mixed. In this work, full external calibrations could be obtained for the both the NF and low UF MWCO PEG mixtures since there were negligible ‘cross-over’ or ‘combined’ peaks from the component commercial grade PEGs (i.e. peaks from oligomers that are present in more than one of the commercial PEGs, whose peak area is therefore a combination of the contributions from the concentration of that oligomer in both of the commercial PEGs). The deconvolution of the concentration attributable to these ‘combined’ peaks is difficult to accurately estimate. Although this issue was not significantly present in this work, this may not be the case for other users of this method (acknowledging that results can depend on a range of factors, including the exact

HPLC system and ELSD detector that is used), so two different calibration and MWCO curve calculation methods are outlined below, one for when there are no ‘combined’ peaks and one for when there are to cover all eventualities.

If there are no combined peaks, like in this work, the concentration of each peak and each PEG oligomer in the NF and low UF mixture chromatogram can be attributed to the commercial PEG that it came from and so the concentration of each peak can be calculated using equation 3:

$$C_i = \frac{A_i}{[\sum_{i=1}^n A_i]_{commPEG x}} C_{commPEG x} \quad (3)$$

Where:

C_i = concentration of each individual oligomer’s corresponding to peak i

$C_{commPEG x}$ = concentration of commercial grade PEG (commPEG) x (the one which contains oligomer peak i)

A_i = the area of the individual oligomer’s peak i

$(\sum_{i=1}^n A_i)_{commPEG x}$ = the total area of all peaks in commercial grade PEG x

n = total number of oligomer peaks in the HPLC chromatogram.

Using this, different concentrations of the NF and low UF mixtures were run using the HPLC-ELSD method and calibration curves (of oligomer concentration versus peak area) were established for every oligomeric peak in the NF and low UF PEG mixtures. The linear calibration range was established and calibration curves were fitted to these linear regions (see Supplementary Material A for details). From this, it was established that the peak response for the NF MWCO mixture is linear for concentrations from 50 to 400 mg L⁻¹ and for the low UF MWCO mixture the calibrations are still linear at 800 mg L⁻¹ making this

method more useful over a wider range of PEG concentrations. Both linear ranges are sufficient for the use of these calibrations to calculate and determine MWCO curves and the MWCO for NF and low UF membranes. This is a good result for an ELSD method, since the only notable disadvantage of using an ELSD method is that the linear response range with changing concentration is sometimes quite limited, making the ELSD results difficult to use [41].

As mentioned above, it is acknowledge that the above method may not be able to be used if the commercial grade PEGs have a number of oligomeric peaks in common, making the deconvolution of the concentration attributable to these ‘cross-over’ or ‘combined’ peaks difficult to accurately estimate. However, in this case, the rejection of the oligomers for the NF MWCO PEG mixture can still be calculated by making one assumption: that the concentration-area calibration line for the oligomers goes through the origin (zero-zero). This means that the calibration equation is assumed to be of the form:

$$C_i = B \cdot A_i \quad (4)$$

Where B is a constant. The calibration lines in Supplementary Material A show that the assumption made is good, with all calibration lines approximately going through the origin, with negligible offset.

Rejection for the MWCO curve therefore can be calculated directly from the feed and permeate HPLC chromatogram peak areas, since constant B will be the same for the same peak so long as the area response is within the linear range:

$$\text{Rejection } R, \% = \left(1 - \frac{A_{i, \text{permeate}}}{A_{i, \text{feed}}} \right) \times 100\% \quad (5)$$

Where:

$A_{i, \text{permeate}}$ = area of oligomer i in permeate HPLC chromatogram of NF PEG mixture

$A_{i, feed}$ = area of oligomer i in permeate HPLC chromatogram of NF PEG mixture.

To establish the linear range of the calibration, to ensure that equation 4 is valid, one must ensure that the calibration is linear for the oligomer that has the highest individual component concentration in all four of the commercial grade PEGs used. These oligomers are easily identified since they have the largest peaks from their respective commercial grade PEGs. Figure 4 shows that these largest peaks are not ‘combined’ peaks and so a concentration versus area calibration curve can be easily established for these oligomers/peaks from HPLC chromatograms of the NF PEG mixture at different concentrations, (a variation on equation 3):

$$C_i = \frac{A_i}{[\sum_{i=1}^n A_i]_{NF\ PEG\ mix}} [C_{total}]_{NF\ PEG\ mix} \quad (6)$$

Where:

$$\begin{aligned} [C_{total}]_{NF\ mix} &= \text{total concentration of all PEG oligomers in the total NF mixture} \\ &= \frac{\sum_{x=1}^z m_x}{V_{total}} = \frac{m_{PEG200} + m_{PEG400} + m_{PEG600} + m_{PEG1000}}{V_{total}} \end{aligned} \quad (7)$$

$[\sum_{i=1}^n A_i]_{NF\ PEG\ mix}$ = the total area of all peaks in the total NF mixture

m_x = mass of commercial grade PEG x

V_{total} = total volume

z = total number of commercial grade PEGs used in the NF mixture (= 4 in this work).

3.3 Benchmarking of the MWCO using characterized commercially available membranes

Fig. 7 shows the resulting HPLC chromatograms of the feed, retentate and permeate from filtering the NF and UF PEG mixtures through two different commercially available membranes - Filmtec NF270 and Hydracore 7450. In both filtration ranges, the permeate peaks show a lower intensity than the peaks of the feed, showing the membrane selectivity for the PEG MWCO mixture is as expected: higher MW oligomers are rejected by the membrane (i.e. retained) and lower MW oligomers are permeated, with the retentate peaks having higher peak intensities than the feed and permeate (as the feed solution has been concentrated through the permeation of solvent and lower MW oligomers).

<Fig. 7 here>

Using this technique, the MWCO of a range of commercial membranes was measured: rejection of the oligomers versus their MW is given in Fig. 8. The MWCO extrapolated from this is given in Table 6, along with flux and the nominal MWCO given by the manufacturer. In all filtrations, the membranes performed as expected – for example, the flux through the membrane was lower in presence of PEGs than with pure deionized water.

Fig. 8 and Table 6 shows the MWCO measured is close to previously measured by a manufacturer's or in another study reported in the available literature MWCO, despite the different tests that would have been used to obtain these. Error ranges in the MWCO values measured in this study were calculated by determining the mean MW values at three different extrapolations of the cut-off curves to the best possible fit lines which intersect at 90% rejection. The validity of the developed MWCO method is well demonstrated by several of these results. For example, the MWCOs determined for the Dow FilmtecTM NF and NF270 membranes mirrors the findings in ref [6] which found that NF 270 had a higher MWCO. NF

270 has a looser structure with larger pores and a higher porosity than NF.

There are slight differences in the MWCO values reported from literature (Table 6), which are most likely attributed to differences in the interactions of the different solutes (i.e. glucose [42], dye [43], natural organic matter (NOM) [44], poly diallyldimethylammonium chloride (PDADMAC) [6] and dimethyl aminoethyl acrylate (CoAA) [6]) used in their MWCO tests compared to the PEG mixture used here. The largest variation is for the Dow Filmtec™ NF 270 membrane, with a MWCO of 1110 g mol⁻¹ from ref. [6] compared to 330 ± 4 g mol⁻¹ from the method in this work. The value in this work is much closer to the manufacturers estimate of 400 g mol⁻¹ however, most likely indicating that the estimate in ref. [6] is incorrect. Differences in feed concentration may also be a cause of a difference in MWCO values, where higher concentrations will skew the MWCO higher. This is shown in ref. [45], where in the MWCO determination of MPF-44 (manufacturers MWCO of 250 g mol⁻¹) safranin O (MW 350 g mol⁻¹) at 0.01wt% had a lower rejection (68%) than at 1wt% (rejection = 94%), probably due to concentration polarisation and/or fouling at the higher concentration. The use of charged or polar organic solutes such as eosine, congo red [46], glucose and sucrose [47], would also produce a difference in measured MWCO, since if the membrane itself has an appreciable surface charge there will be a double layer interaction with these solutes, an interaction of that does not exist with the non-polar PEGs used in this study. This can result in a higher or lower MWCO compared to the method in this work [44]. Different molecules may also produce different MWCOs to PEGs due to differing macromolecular chain deformation and orientations during filtration [48].

Overall, the method developed in this work gave MWCO values within 3% (Dow Filmtec™: NF) to 20% (Koch: TFC-SR100) of the manufacturers values with good agreement to literature values, verifying the accuracy of the method. Therefore more accurate MWCO values can be obtained when using the method developed in this work compared to

comparable MWCO methods [2, 3, 9]. This result also significantly improves on the PEG HPLC-ELSD MWCO method reported in ref. [21] where the MWCO value of a commercial organic solvent resistant NF membrane tested with an oligomer mixture from PEG 600 was shown to differ considerably from the nominal MWCO specified by the manufacturer. It is also improves on the work reported in ref. [2], which suffered from pore blocking, giving a MWCO value lower with a PEG mixture than when single PEGs where used.

So overall, compared to these past methods, MWCO can be more accurately and precisely determined over a wider MW range than previously possible with a one-filtration aqueous based method, since high-resolution PEG oligomer peaks can be obtained with known individual MWs separated by only 44 g mol^{-1} over a wider range of MWs than previously achieved.

<Fig. 8 here>

<Table 6 here>

4. Conclusions

A refined one-filtration method for the determination the MWCO of aqueous based NF and UF membranes using a broad range of MW polyethylene glycols was developed and verified as accurate. With this method, MWCO can be more precisely determined over a wider MW range than previously possible with a one-filtration aqueous based method, with individual MWs separated by only 44 g mol^{-1} and from 106 to 1250 g mol^{-1} for the NF MWCO range analysis and from 634 to 1646 g mol^{-1} (followed by 4000 and 6000 g mol^{-1}) for the low UF MWCO range analysis. The key to the method is a reverse phase HPLC-ELSD PEG oligomer separation and quantification method that gives a high chromatographic resolution of individual PEG oligomers between the MWs of 106 and 1646 g mol^{-1} and clustered

quantification based on average MW of PEG mixtures above this. The method is also likely to be more economic than previous methods: it is achieved on a widely available low cost C8 column coupled with an ELSD detector at 60°C and a mixture of cheap PEGs can be used in just one filtration meaning less time and resources are now needed to determine MWCO.

The method gave MWCO values within 3% (Dow Filmtec™: NF) to 20% (Koch: TFC-SR100) of the manufacturers and literature values for Koch MPF34, MPF36, MPF44 and TFC-SR100 and Hydranautics 7450 membranes with good agreement to literature values, verifying the accuracy of the method. The slight difference in MWCO values were due to the different types of solutes used to determine the MWCO compared to the manufacturers and in the literature studies.

Given the above advantages and verifications, this method can now effectively replace the previously required time consuming and costly multiple filtrations of individual PEG oligomers and other compounds for the determination of membrane MWCO for aqueous applications.

Acknowledgments

The authors would like to acknowledge the financial support of the University of Auckland Faculty Research Development Fund, Grant 3622753/9571, the Department of Chemical and Materials Engineering at the University of Auckland and the Ministry of Higher Education of Malaysia and the National University of Malaysia for the PhD scholarship. The authors would also like to thank the following people for their help in this work: Peter Buchannan, Allan Clendinning, Laura Liang, Jessie Mathew and Cecilia Lourdes.

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Fig. 4. HPLC chromatograms showing the relationship between the oligomer peaks in the different commercial PEGs and the same peaks in the NF and low UF PEG mixtures, highlighting the average MW (M_n) in the different sets of chromatograms all at 400 mg L⁻¹ (i) upper: HPLC chromatograms of the each of the commercial PEGs used in the NF range mixture (PEG 200 to 1000), lower: HPLC chromatogram of the NF range PEG mixture; (ii) upper: HPLC chromatograms of the each of the separated commercial PEGs used in the low-UF range mixture (PEG 1000 to 1500), lower: HPLC chromatogram of the low UF range mixture.

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Fig. 8. MWCO curve for commercial membranes using the PEG HPLC-ELSD method developed (i) NF range; (ii) low UF range.

Table 1

Commercial membranes used in MWCO characterisation.

Membranes	Supplier	Type
Koch: MPF34	Koch Membrane Systems	NF
Koch: TFC-SR100	Koch Membrane Systems	NF
Koch: TFCS	Koch Membrane Systems	NF
Koch: MPF44	Koch Membrane Systems, USA	NF
Dow Filmtec™: NF	Dow Filmtec™, USA	NF
Dow Filmtec™: NF270	Dow Filmtec™, USA	NF
Koch: MPF36	Koch Membrane Systems	UF
Hydranautics 7450	Hydranautics, USA	UF

Table 2

PEG oligomer mixtures used in: (i) the MWCO mixture of commercial grade PEGs with respective average molecular weight given by the manufacturer (M_n), and (ii) the purer grade standard PEG solution with respective highest peak molecular weight (M_p) as determined by the manufacturer.

Chemical	MWCO mixture from commercial grade PEGs		Purer grade PEG standards	
	Supplier	M_n (g mol ⁻¹)	Supplier	M_p (g mol ⁻¹)
PEG 200	Sigma-Aldrich, USA	200	Fluka, Switzerland	232
PEG 300	-	-	Fluka, Switzerland	330
PEG 400	Sigma-Aldrich, USA	400	-	-
PEG 600	Sigma-Aldrich, USA	570 – 630	Fluka, Switzerland	630
PEG 1000	Sigma-Aldrich, USA	950 – 1050	Fluka, Switzerland	980
PEG 1500	Applichem, GmbH	1500	Fluka, Switzerland	1460
PEG 4000	Applichem, GmbH	4000	-	-
PEG 6000	Scharlau, Barcelona	6000	-	-

Table 3

Final HPLC gradient profiles for the elution of PEG mixtures at different range of molecular weight.

PEG MW range	Elution time (min)	Gradient (% Acetonitrile)	Gradient (% Water)
Low MW range	0	15	85
PEG 200 - 1000	42	30	70
(NF)	45	80	20
High MW range	0	15	85
PEG	2	25	75
1000 - 6000	20	25	75
(Low UF)	62	50	50
	65	20	80

Table 4

Molecular Structure of Linear Chain PEG Oligomers and the relationship between number of repeating units, n, the PEG oligomer and the commercial PEG oligomeric mixture that this oligomer is part of.

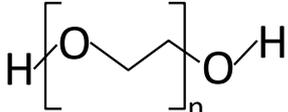
Molecular structure:		
		
Structural formulae:		
$H-(OCH_2CH_2)_n-OH$		
n-value	PEG Oligomer MW (g mol ⁻¹)	Corresponding Commercial PEG
1	106	PEG 100
2	150	PEG 150
3	194	PEG 200
4	238	
7	370	PEG 400
8	414	
12	590	PEG 600
13	634	
21	986	PEG 1000
22	1030	
32	1470	PEG 1500
33	1514	
89	3978	PEG 4000
90	4022	
134	5958	PEG 6000
135	6002	

Table 5

Summary of the identified molecular weight of the different peaks in the NF range of the MWCO PEG analysis obtained from the two different external calibration methods and the finalized.

Retention time (min) (NF range)	4±0.25	5±0.25	6±0.25	11.5±0.5	13.5±0.5	29±0.5
Commercial PEGs' M_n (g mol ⁻¹)* (Summarized from Fig. 4(i))	200	-	400	570 – 630	-	950 – 1050
Purer Standard PEG M_p (g mol ⁻¹)* (Summarized from Fig. 5)	232	330	-	-	628	982
Finalised PEG mixture oligomers' MW (g mol ⁻¹) (Summarized from Fig. 6(i))	238	326	370	546	590	986
Retention time (min) (Low UF range)	12±0.5		31±0.5		50±0.5	55±0.5
Commercial PEGs' M_n (g mol ⁻¹)* (Summarized from Fig. 4(ii))	950-1050		1500		4000	6000
Finalised PEG mixture oligomers' MW (g mol ⁻¹) (Summarized from Fig. 6(ii))	942		1514		4000	6000

*Values given by the respective manufacturers.

Table 6

Membrane separation properties (flux and MWCO) of the different commercial membranes obtained from dead-end filtration test.

Membranes	Type	Flux in water (L m ⁻² h ⁻¹)	Flux in PEGs (L m ⁻² h ⁻¹)	MWCO Measured at 90% rejection (g mol ⁻¹)	Nominal MWCO supplied by Manufacturer (g mol ⁻¹)	MWCO Obtained from Literature (g mol ⁻¹)
Koch: SelRO [®] MPF-34	NF	49.4	48.4	215 ± 5	200	180 [42] (at 95% rejection of glucose)
Koch: TFC-SR100	NF	164.7	139.7	235 ± 5	200	<180 [49] (using lactose marker test by Fluids Systems)
Koch: SelRO [®] MPF-44	NF	49.9	42.3	260 ± 14	250	351 [45] (at 94% rejection of safranin O - 1wt% feed)
Dow Filmtec [™] : NF	NF	181.3	155.1	305 ± 4	200-300	290 [44] (90% rejection of natural organic matter)
Dow Filmtec [™] : NF270	NF	404.2	214.4	330 ± 4	400	1110 [6] (at 90% rejection of PDADMC* & CoAA**)
Koch: SelRO [®] MPF-36	UF	1297.8	850.3	1140 ± 8	1000	800 [43] (98% rejection of Dye)
Hydranautics7450	UF	321.3	76.9	1075 ± 16	700 – 1000	646-697 [46] (88-100% rejection of eosine & congo red)

*poly diallyldimethylammonium chloride (PDADMAC), **dimethyl aminoethyl acrylate (CoAA)

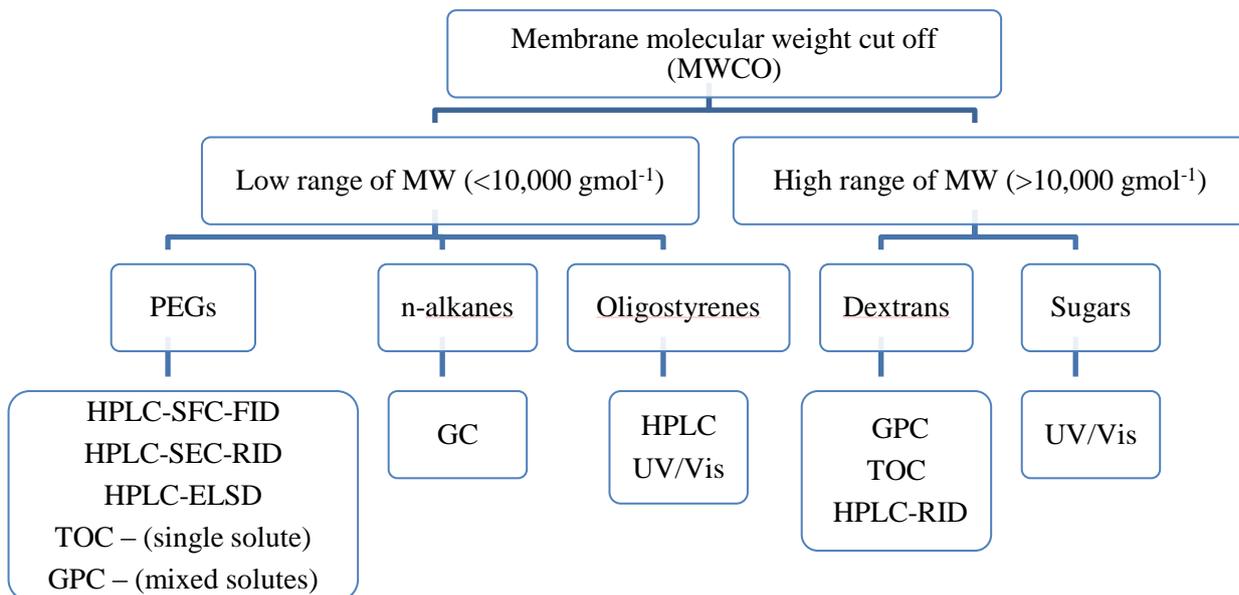


Fig. 1. Membrane selectivity measured by different analytical method for its molecular weight cut-off (MWCO).

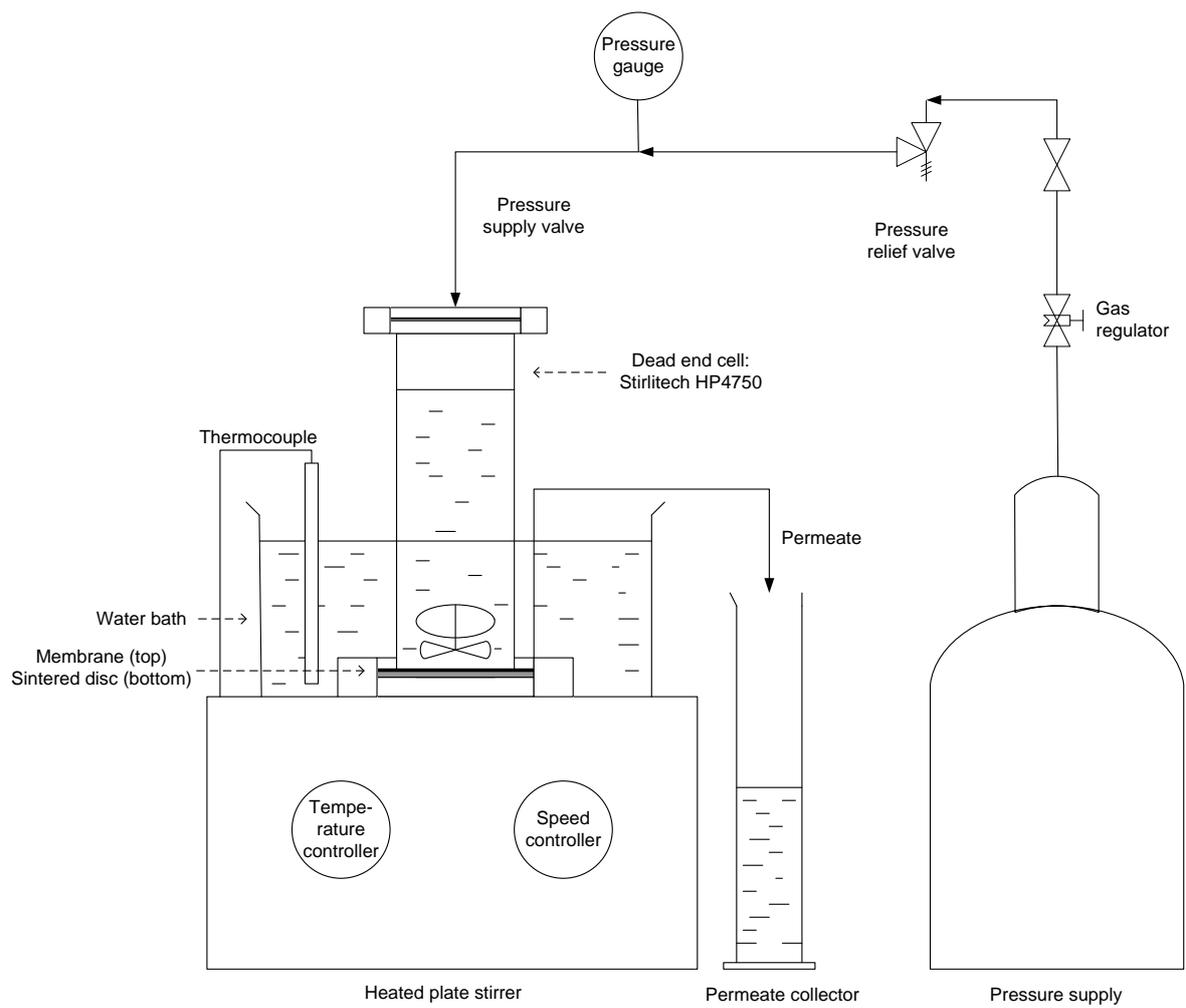


Fig. 2. Schematic diagram of the dead-end permeation cell.

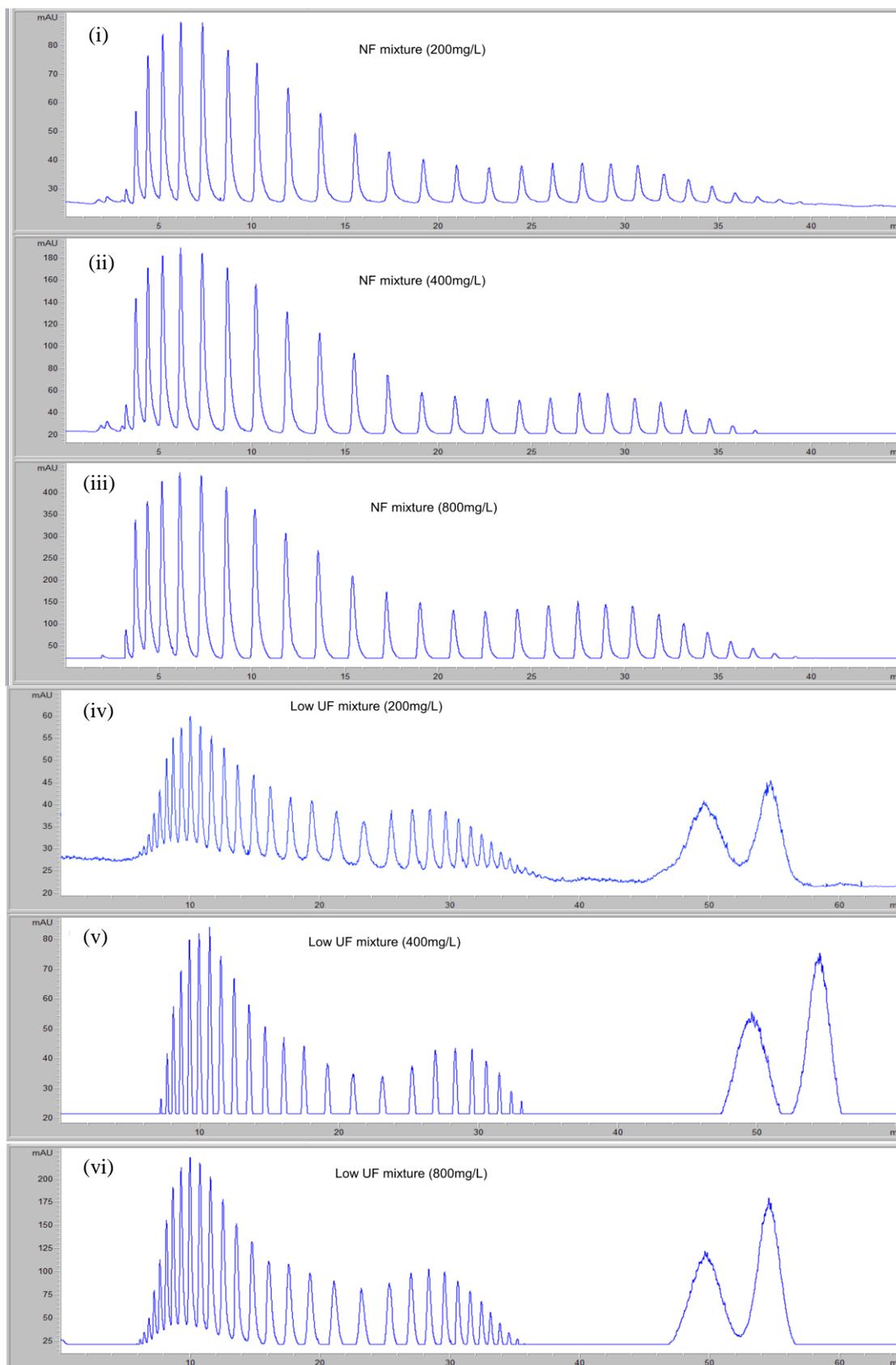


Fig. 3. Separated PEG oligomer peaks from the HPLC-ELSD method on the two different

PEG mixtures at different concentrations. NF range mixture from PEG 200, 400, 600, 1000 at:

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1500, 4000 at: (iv) 200 mg L⁻¹, (v) 400 mg L⁻¹ and (vi) 800 mg L⁻¹.

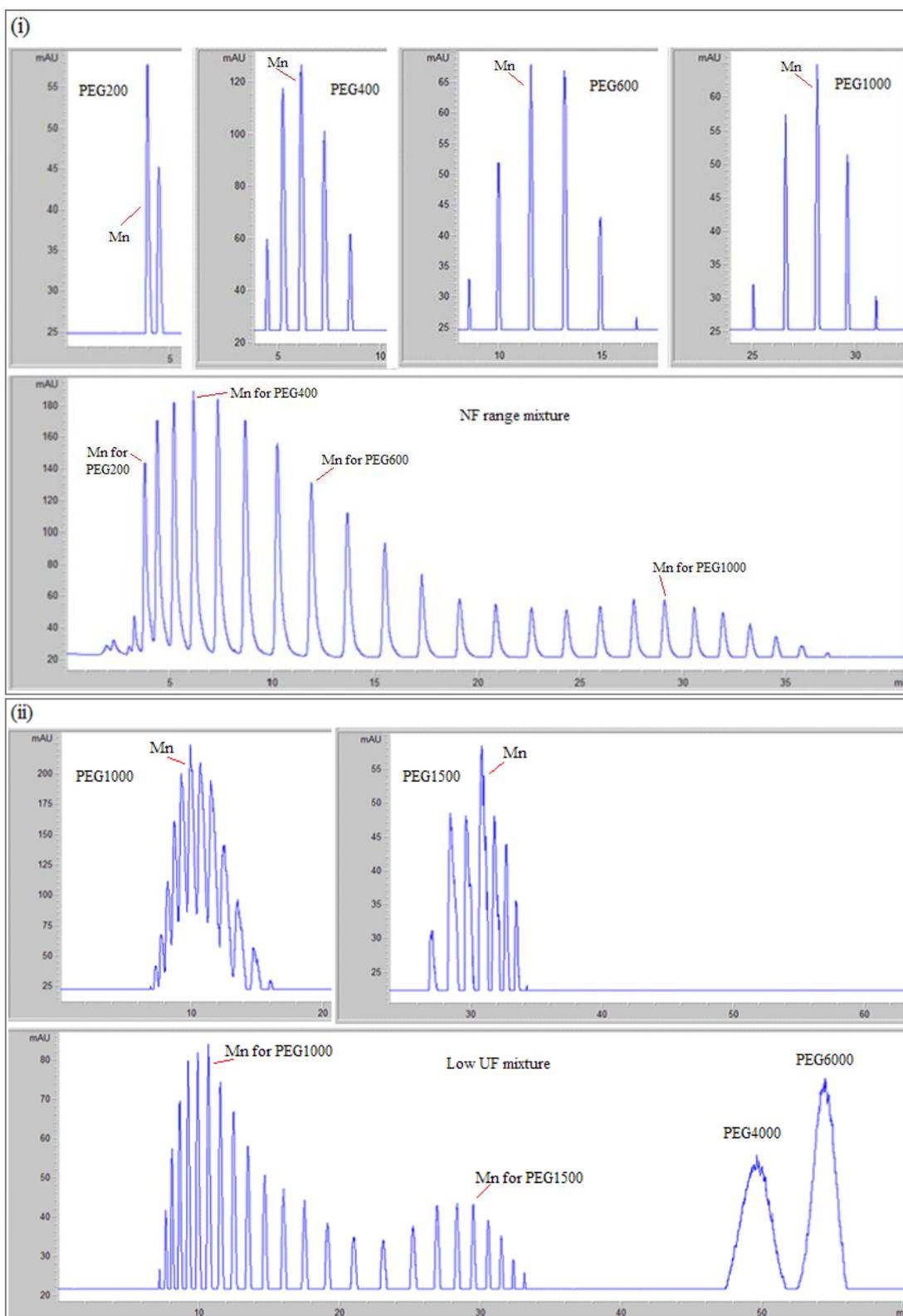


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upper: HPLC chromatograms of the each of the commercial PEGs used in the NF range mixture (PEG 200 to 1000), lower: HPLC chromatogram of the NF range PEG mixture; (ii) upper: HPLC chromatograms of the each of the separated commercial PEGs used in the low-UF range mixture (PEG 1000 to 1500), lower: HPLC chromatogram of the low UF range mixture.

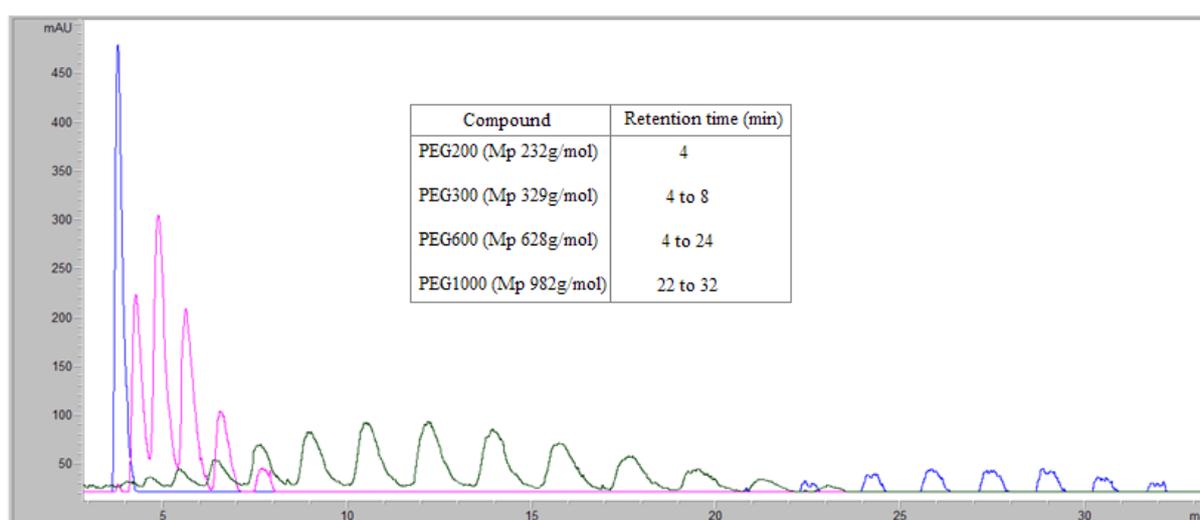


Fig. 5. The PEG standards with M_p 232-1460 $g\ mol^{-1}$ analyzed using the HPLC-ELSD method developed.

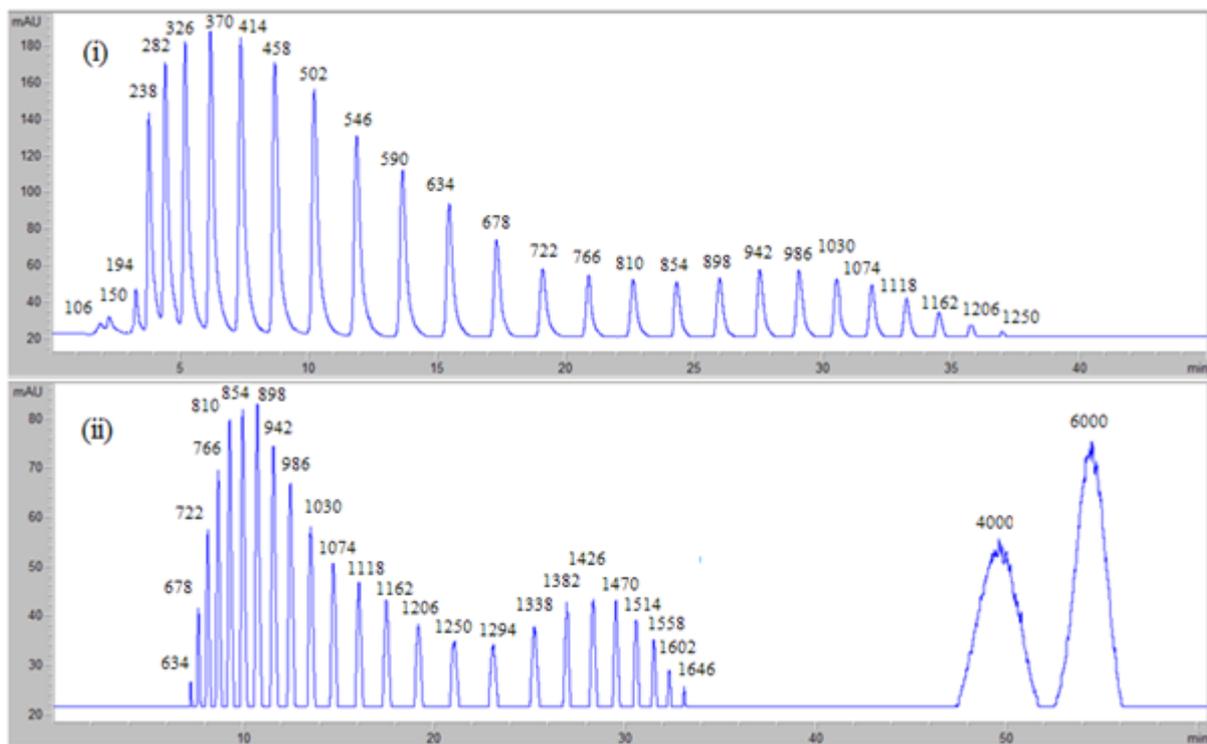


Fig. 6. Identification of individual PEG oligomers mixture from the: (i) NF range (ii) low UF range.

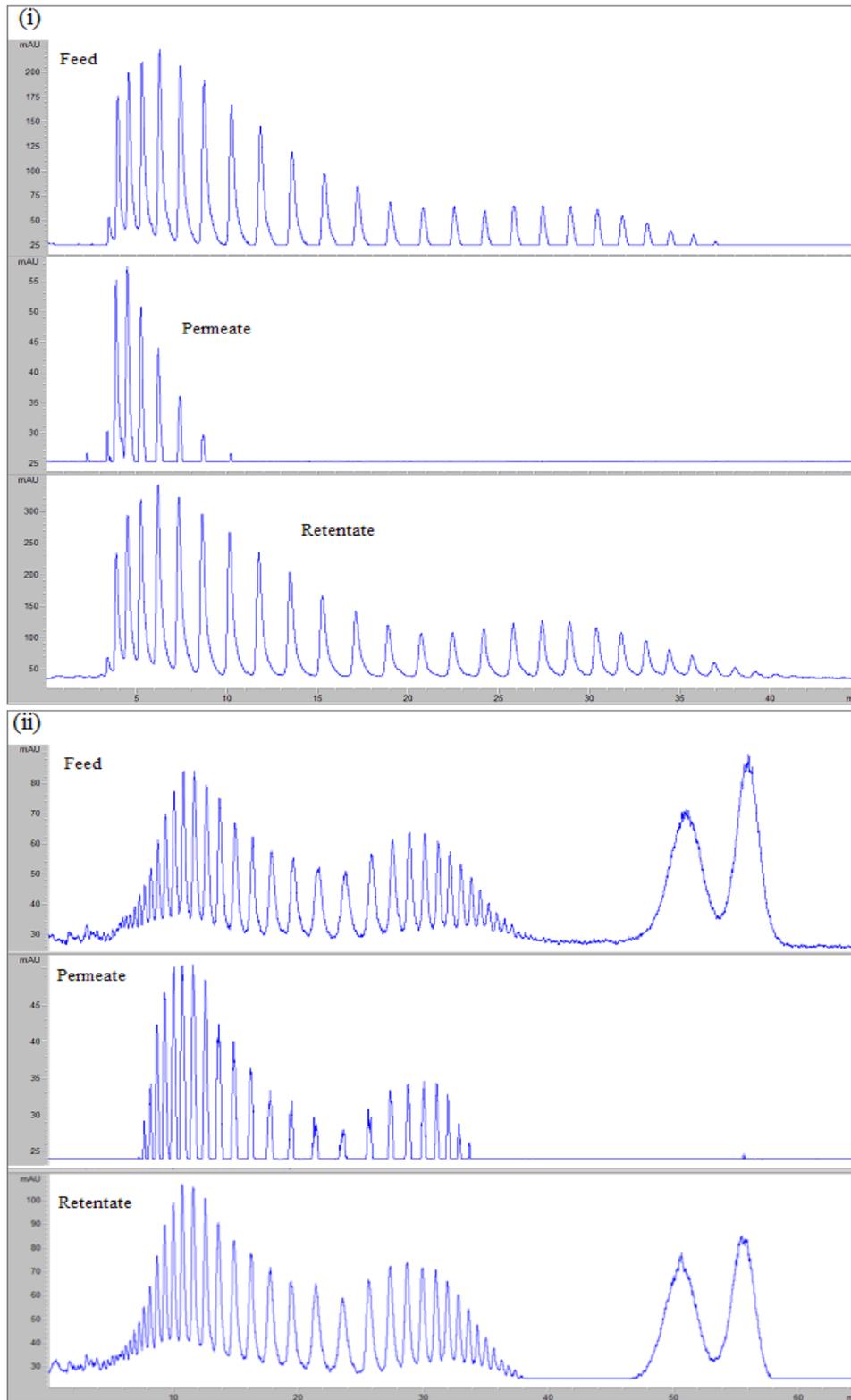


Fig. 7. HPLC chromatograms of the feed, permeate and retentate from (i) NF range PEG mixtures separated by the Filmtec™ NF270 Membrane; (ii) low UF range PEG mixtures separated by the Hydracore Hydranautics7450 Membrane.

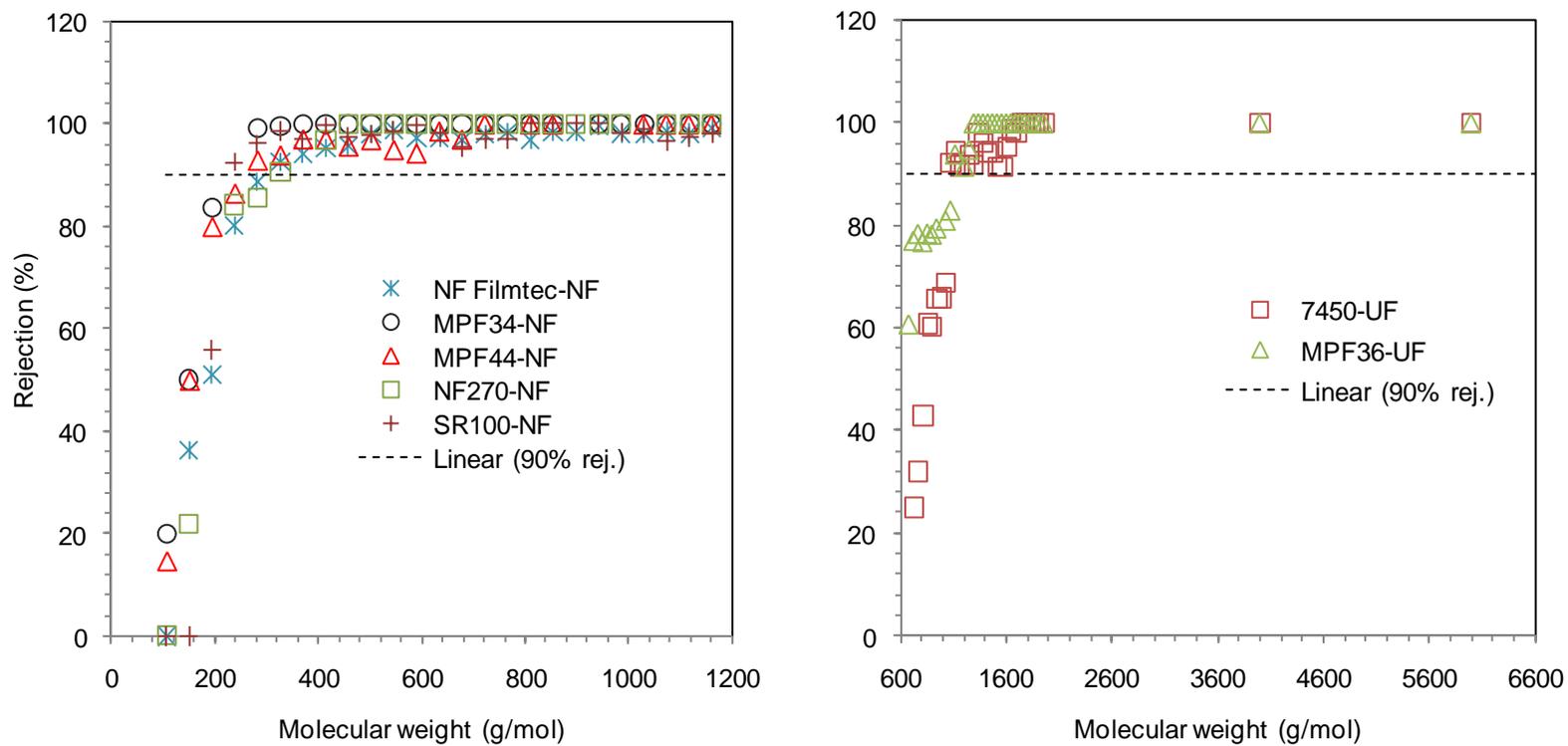


Fig. 8. MWCO curve for commercial membranes using the PEG HPLC-ELSD method developed (i) NF range; (ii) low UF range.