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A wide range and high resolution one-filtration molecular weight cut-off method for aqueous based nanofiltration and ultrafiltration membranes

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Abstract

A new and superior one-filtration method for the determination of the molecular weight cut-off (MWCO) of aqueous based nanofiltration and ultrafiltration membranes has been developed using the widest range of polyethylene glycol oligomers as MWCO probes of any MWCO method so far. This method was enabled by a new, high resolution oligomer separation and detection using high performance liquid chromatography (HPLC) coupled with an evaporative light scattering detector (ELSD). The refined method can determine the MWCO of membranes over a MW range from 678 to 4594 g mol^{-1} with a molecular weight difference of just 44 g mol^{-1} and a bonus further one point extension to 6000 g mol^{-1} – giving the widest range and most precise difference of MWs that can be resolved of any single filtration MWCO method that exists. MWCO determination of five commercial membranes from GE Osmonics™ and Millipore showed good agreement with manufacturer and literature values, confirming the accuracy of the method. As this new method has significant advantages over all other existing aqueous MWCO determinations (i.e. single filtration, higher resolution over a wider MW range, low cost MWCO molecular probes), it is suggested that it could be adopted as the new standard for determining aqueous MWCO over a MW range from 678 to 6000 g mol^{-1}.

1   Introduction

Pressure driven membrane separations have been widely applied in many industries as they enable separations to become more energy efficient and environmental friendly [1, 2]. Membranes are selective semi-permeable barriers that are used to produce purified streams and therefore the worth of a membrane is in its productivity (normally quantified as flux) and selectivity. Selectivity for pressure driven membrane processes such as nanofiltration (NF) and ultrafiltration (UF) is typically quantified and benchmarked as the molecular weight cut-off (MWCO),[3] which is defined as the molecular weight (MW; also known as molecular mass) that a 90% rejection of the filtered solutes is obtained. A reliable technique for measuring MWCO values is crucial for end users to make an appropriate choice of membrane in order to buy, test and apply over the wide range of applications, solvents and solutes that are wanted for a particular membrane [4, 5].

A range of methods and MWCO molecular probes currently are used, including styrene oligomers [4, 6, 7], polyethylene glycols (PEGs) [1, 2][2, 8-10], dextrans [11-16], alkanes [17, 18], sugars [19, 20], dyes[21], acids [9], and others [20, 22-24]. The MWCO of UF membranes can also be determined by liquid–liquid displacement porometry (LLDP) method [25]. A literature comparison of MWCO probes for aqueous filtrations can be found in Rohani *et al.* [1, 2] and so will not be repeated here. Of importance are the limitations of these existing methods so these can be addressed:

(1) The detection of multiple compounds in a single filtration is difficult to accomplish, thus most of the methods require multiple and repetitive test filtrations of individual solutes to obtain the MWCO curve, which is both time consuming and costly compared to a single filtration method. [2, 4, 24, 26].

(2) Of the available MWCO molecular probes, pure alkanes and dextrans are only commercially available with MWs of below 400 g mol^{-1} and above 1000 g mol^{-1}, respectively. Styrene oligomers are expensive in comparison to all other molecules used and therefore this limits their application at a larger scale. Dyes are mainly charged molecules and therefore will also potentially be rejected by Donnan Exclusion, which does not reflect the MW (size/mass) based separation that MWCO should primarily reflect. Furthermore, it is not easy to source a suitable variety of dyes with similar molecular structures that have a similar interaction with the membrane. Other solutes,

like alkane and polypropylene glycol, have limited solubility in water, especially at higher MWs, which limits their use [1, 21].

(3) Other methods, such as liquid–liquid displacement porometry is used for UF membranes and was examined for MWCOs between 5 kDa to 100 kDa [25]. However the method is less accurate in the low UF range that is aimed for in this paper and has not been extended accurately into the NF range. Therefore an alternative method is still needed.

(4) Some of the methods are for organic solvent based separations and limited to the NF (200-2000 g mol^{-1}) range and due to limited water solubility cannot be directly employed in aqueous systems [2, 4, 26].

(5) For aqueous systems, many of the methods that have been developed only have a limited range of MWs that can be probed, with many mainly focused on and/or just above the NF range [1, 27, 28]. This limits the potential membranes that can be screened and characterised, for example low MWCO UF membranes have attracted considerable attention as they are widely used in oil/organic solvent separation [29], the food industry for sweetener purification [30], metal removal [31] and drinking water treatment [32]. Moreover, when a new membrane is synthesised and the MWCO is unknown, a method that allows a wide range of MWs to be tested with relative precision and resolution would allow a faster characterisation time, which in turn provides faster feedback in order to speed up development time – something needed for high throughput synthesis of membranes for example [33]. Consequently, it is of importance to develop an approach for the MWCO determination of both NF and low UF membranes over the widest possible MW range with the highest possible resolution between adjacent MWs.

Therefore, this research aims to develop a reliable, cost effective, high resolution, single filtration MWCO evaluation method covering a wider MW range than any other MWCO method for aqueous based NF and low MWCO UF membranes.

2   Materials and Methods

2.1   Materials

Table **1** gives the MWs and suppliers for the commercial PEG and purer PEG standard used in the method. The properties of commercial membranes used as well as the filtration pressures are provided in

Table **2**. GE Osmonics™ (GE, GK, GH) and TriSep UA60 were purchased from Sterlitech (US). Millipore disc membranes (Ultracel PLAC04310, Ultracel PLBC04310) were purchased from Sigma-Aldrich (UK). GE Osmonics™ GE and Millipore Ultracel PLAC04310 are NF membranes while GE Osmonics™ GH, GE Osmonics™ GK, TriSep UA60 and Millipore Ultracel PLBC04310 are UF membranes. Acetonitrile (HPLC grade) and Rose Bengal (dye content 95%) were obtained from Sigma-Aldrich (UK). All solutions were prepared with deionised (DI) water produced from an ELGA deioniser (PURELAB Option).

Table 1 Supplier and MW of the commercial grade PEGs and purer grade PEG standard used

Chemical	Supplier	Manufacturer specified average MW (g mol^{-1})
PEG 1000 (Commercial grade)	Alfa Aesar (UK)	950-1050
PEG 1000 (Purer grade)	Fluka (Switzerland)	950-1050
PEG 1500 (Commercial grade)	Alfa Aesar (UK)	1450-1500
PEG 2000 (Commercial grade)	Alfa Aesar (UK)	1800-2200
PEG 3000 (Commercial grade)	EMD Millipore (UK)	3000
PEG 4000 (Commercial grade)	Alfa Aesar (UK)	3600-4400
PEG 6000 (Commercial grade)	Alfa Aesar (UK)	5400-6600

Table 2 Characteristics of the commercial membranes used to benchmark the new PEG MWCO technique

Membranes	Nominal MWCO range (g·mol⁻¹)	Membrane materials	Type	Manufacturer recommended filtration pressure (bar)	Applied pressure (bar)
GE Osmonics™ GE	1000 [34, 35]	Composite Polyamide	NF	27.6	25
GE Osmonics™ GH	1000-2500 [30, 34, 36, 37]	Thin Film	UF	10.3	10
GE Osmonics™ GK	2000-3500 [30, 34, 36, 38]	Thin Film	UF	5.2	5
TriSep UA60	1000-3500 [39]	Polypiperazine-amide	UF	7.6	7
Millipore Ultracel PLAC04310	1000 [40]	PLAC cellulosic (regenerated cellulose)	NF	≤4.8	4
Millipore Ultracel PLBC04310	1000-3000* [41, 42]	PLBC cellulosic (regenerated cellulose)	UF	≤4.8	4

Commercial grade PEGs were selected as MWCO molecular probes since they are available in a wide range of MWs from a number of different manufacturers, are low price compared to other MWCO molecules (e.g. styrenes), are electrically neutral, are soluble in water over a wide range of concentrations and have minimum chemical interactions with membranes compared to more polar and charged molecules [1, 2]. These commercial grade PEGs were dissolved in deionised water to obtain a PEG oligomer mixture solution with a wide MW range. Two different PEG mixture solutions were prepared:

(1) The 'feed solution' was used in the filtrations and was: 600 mg L^{-1} for PEG 1000 and 2400 mg L^{-1} for PEGs 1500 to 6000. Note that the concentration of the PEG 1000 was three times lower than the other PEGs used in the mixtures since its peak response in the DAD detector was 3 times higher when comparable concentrations and so was used at this lower concentration to ensure peak heights and areas were similar across the entire HPLC chromatogram.

(2) A stock solution that is used to produce the calibration curves, had double the concentration of the feed solution as this is the maximum concentration the retentate can reach if there is 100% rejection of any of the oligomers (since only 50% of the feed volume is filtered in the method used). This stock solution was diluted to produce the different concentrations needed in the external calibration need to determine the concentrations of each oligomer in the resolved HPLC peaks – this is referred to as 'diluted stock solution'. The lowest concentration the stock solution was diluted to for the calibration curve was: 75 mg L^{-1} for PEG 1000 and 300 mg L^{-1} for PEGs 1500 to 6000 as below this concentration, the detector baseline appeared to drift and showed excessive noise. The feed concentration used for the MWCO determination of commercial membranes was 600 mg L^{-1} for PEG 1000 and 2400 mg L^{-1} for PEG 1500 to 6000. Feed concentration was expected to be as low as possible to prevent or at the very least minimise possible concentration polarisation which could affect the MWCO curves and value determined and so the feed concentration applied in the study was comparable to previous publications [2, 43].

2.2   MWCO Analysis method

High performance liquid chromatography (HPLC) coupled with an evaporative light scattering detector (ELSD) was used for the identification of individual PEG oligomers. An ELSD was used since previous work in this research group and elsewhere has

demonstrated that it is the most robust, reliable and sensitive detector for clear detection of different MW PEG oligomers at close MWs if coupled with an appropriate gradient elution [1, 2, 44]. The HPLC apparatus (Agilent 1260 infinity series, Agilent Corporation, USA) consisted of an autosampler (G1329B), a Colcom column oven (G1316A), a Quat pump (G1311B), a degasser and an Agilent data interface. The detection was performed utilising an Agilent ELSD (Agilent 1260 infinity G4260B, Agilent Corporation, USA) with drift temperature set at 60°C. An Agilent Poroshell 120 EC-C18 column (4.6 mm length × 5.0 mm I.D., 2.7 μm particle size) at 50°C was used to achieve the separation of peaks. A flowrate of 1.0 mL min^{-1} was used with a gradient of mobile phase's acetonitrile and water as per Table 3. A sample volume of 50 μL was injected for all analysis. Identification and quantification of PEG oligomer MW and concentration is detailed in Sections 3.2 and 3.3.

Table 3 HPLC gradient for the separation of PEG oligomer

Elution time/min	Gradient A (acetonitrile)/vol. %	Gradient B (water)/vol. %
0	15	85
2	25	75
20	25	75
92	50	50
95	20	80

Calibration curves were established by diluting a stock solution of PEG mixture (1200 mg L^{-1} for PEG 1000, and 4800 mg L^{-1} for PEG 1500 to 6000), covering a wide range of concentrations to give a comprehensive coverage of the expected feed, permeate and retentate concentrations.

2.3   Membrane filtration method

Membrane filtration was performed in a stirred high pressure stainless steel dead-end filtration cell (HP 4750, Sterlitech, USA) using a well-used procedure [1, 45]. Membrane sheets were cut to size using a scalpel to give an active area of 14.6 cm^2. During filtration, the filtration cell was immersed in a water bath at a temperature of 25°C and the contents were kept well mixed at 300 rpm using a magnetic stirrer to minimise concentration

polarisation. The pressure driving force for filtration was provided by nitrogen gas (BOC, UK). As per the well-used procedure, the filtration runs were as follows:[1, 45]

All membranes were initially pre-conditioned with deionised water until a steady state flux was achieved. This consisted of loading the membrane filtration cell with 200 ml of DI water until achieving a stable flux. If the membrane did not achieve a stable flux after 200 ml of water, the membrane disc was discarded (and this was considered a defective disc) and a fresh membrane disc was run. Once a stable flux was reached, the remaining DI water was emptied from the cell and the fluid of interest was loaded: either 50 mL of DI water or the PEG mixture solution and the filtration was run at the pressure required (Table 2) until 25 mL of the permeate was collected. Note that the DI water preconditioning and active filtration (e.g. with the PEG mixture) were separate filtration runs, so the volume of DI water during preconditioning would not affect the feed solution concentration and the results.

Permeate volume versus time was recorded to determine the membrane flux. The solute rejection was calculated using Eq. (1):

$$R_j(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \qquad (1)$$

where R_j is the rejection of membrane, C_f is the PEGs concentration in the feed and C_p is the concentration of PEGs in the permeate. MWCO curves were obtained by plotting the rejection of the individual oligomers in the PEG mixtures against their molecular weights, determining the molecular weight at which a rejection of 90% was achieved.

Six different kinds of commercial NF and UF membranes were chosen to test the actual MWCO range to verify the accuracy and reproducibility of this method (

Table 2).

3 Results and Discussion

3.1 HPLC-ELSD characterisation of the single PEG and PEG mixtures

Each of commercial PEGs was run separately in the HPLC-ELSD method (Fig. 1). Fig. 1 shows that the HPLC method could separate the individual oligomers in each commercial PEG mixture apart from PEG 6000. Higher MW PEG oligomers displayed longer retention times, which is expected since higher MW PEGs with longer non-polar chains tend to be more strongly adsorbed to the C18 column, thus prolonging the elution time. [1]

Overall, the method gave finely resolved PEG oligomer peaks from PEG 1000 to 3000 with straight and stable baselines. The peaks of PEG 4000 were also well separated although a level baseline could not be achieved. PEG 6000 oligomers could not be separation, but eluted separate to the PEG 4000 oligomer peaks and so was treated as a single separate peak with an average MW of 6000 g mol^{-1}. This new method presents a significant improvement on baseline stability and the wide range of MW oligomers resolved and identifiable compared to previous methods [1, 2].
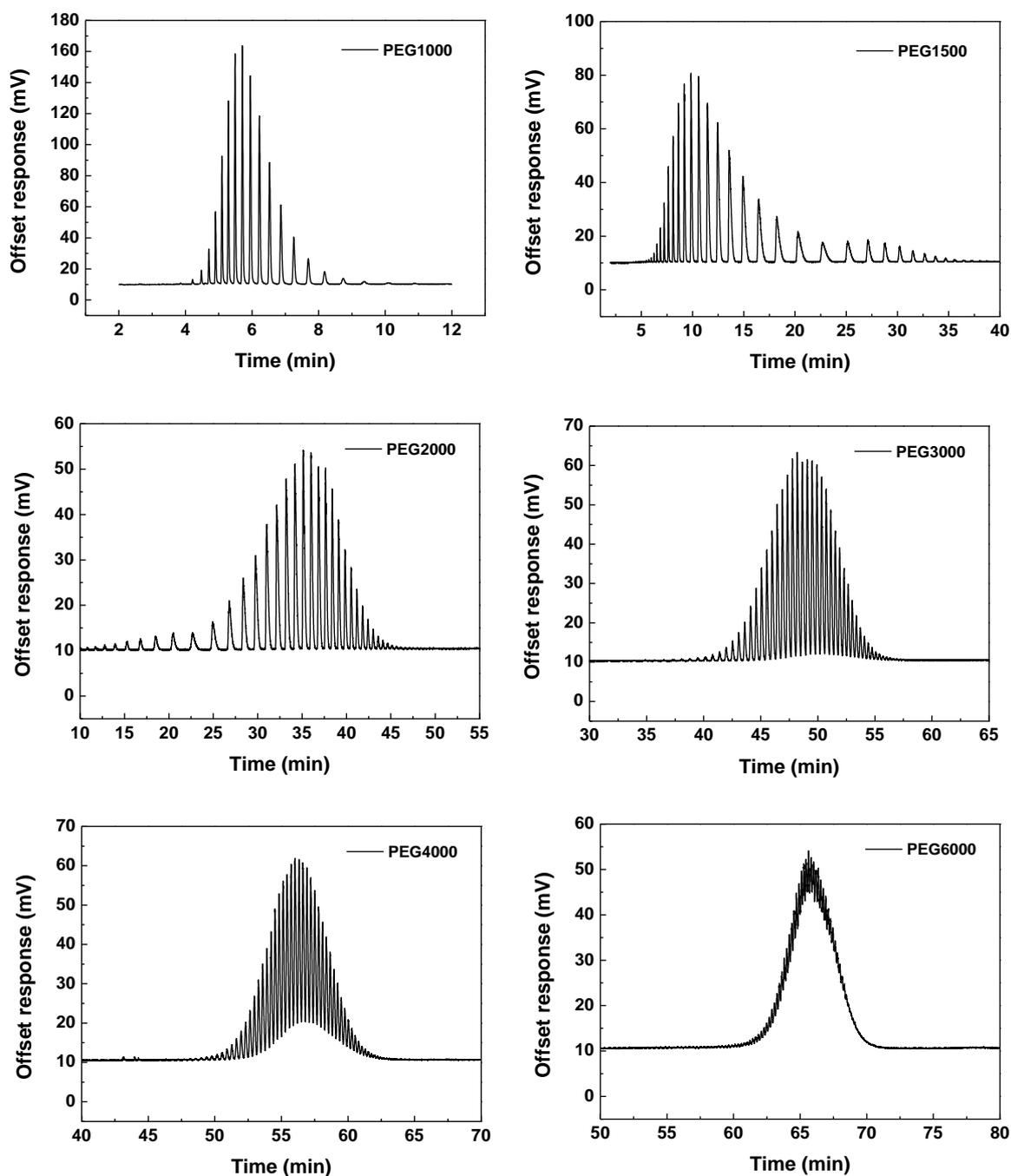
Fig. 1 HPLC-ELSD characterisation of the single PEGs from 1000 to 6000 g mol^{-1}.

When all of these separate commercial PEGs are mixed together and a sample run using the HPLC method, the individual peaks could still be resolved with a clear and stable baseline, as shown in Fig. 2. Varying the concentration of the PEG mixture (for calibration curves – see Supplementary Material), it was found that the peak area increased with increased mixture concentration without losing the baseline resolution. This therefore

shows that the developed HPLC-ELSD method can be used for analysis and quantification of this new wider range of PEG oligomers in a mixture, enabling a new, wider MW range MWCO method to be developed.
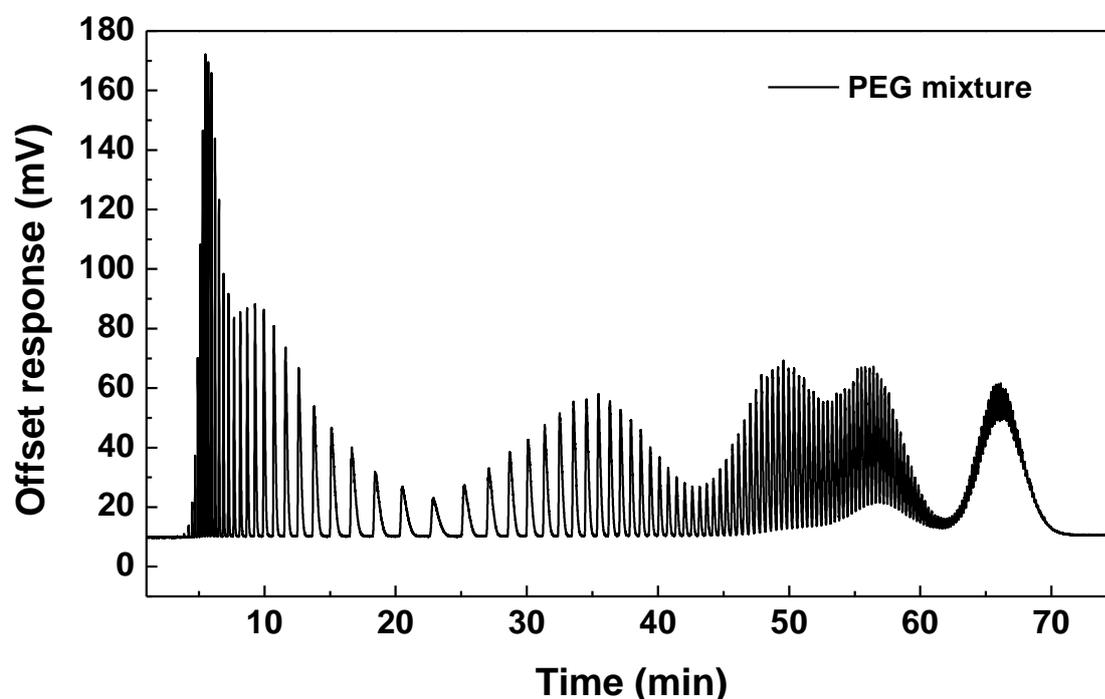
Fig. 2 The oligomer peak separation and detection in the PEG mixture (400 mg L^{-1} for PEG 1000 and 1600 mg L^{-1} for PEG 1500-6000) by the developed HPLC-ELSD method.

3.2   Identification of individual PEG oligomers

In order for this HPLC method to be used in a MWCO method, the precise MW identities of each of the peaks needs to be established. Therefore a purer PEG 1000 standard sample was used to narrow down the MW identities of the peaks within the PEG mixture. In the PEG 1000 standard chromatogram, four consecutive peaks with retention time of 5.73, 5.98, 6.25 and 6.57 min were associated with the first four highest peaks (Table S1 in the Supplementary material). The supplier declared average molecular weight (M_n) range of the purer PEG 1000 standard used was 950 to 1050 g mol^{-1}, which therefore identified these four peaks as corresponding to PEG oligomers with MWs of 942, 986, 1030 and 1074 g·mol^{-1}. In the PEG mixture, the four closest corresponding peaks (with retention times of 5.71, 5.96, 6.23 and 6.53 min) were assigned these MWs (Table S1 and S2 in the Supplementary material).

In order to further guide the MW identification of each peak, the highest response peaks from each individual commercial grade PEG (PEG 1000-6000) were identified in the HPLC chromatogram of the PEG mixture as shown in Fig. 3. These maximal peaks should approximately correspond to the PEG oligomer with the MW closest to the average MW of each of the different commercial grade PEGs used. Although this does not give a direct identification of the oligomers MWs (since there are no pure PEG oligomers with MW of 1000, 1500, 2000, 3000, 4000 and 6000 g mol^{-1} and a range is specified – Table 1), this method however does help guide the assignment of the peaks to those close to that MW [1].
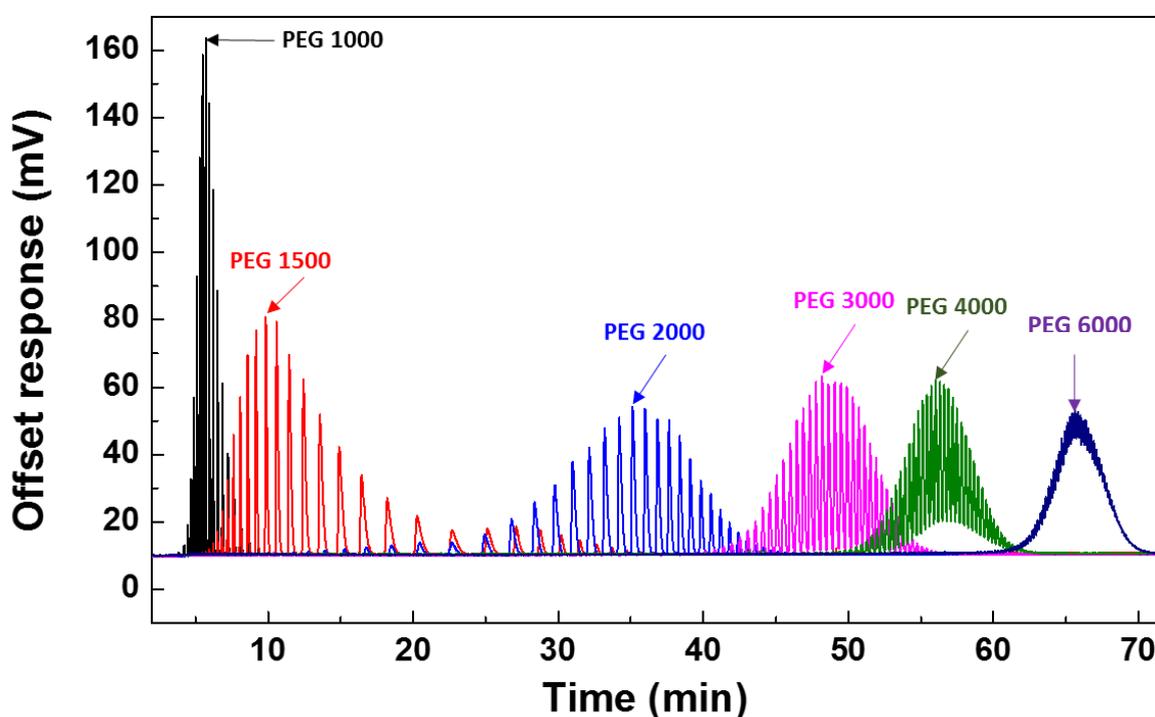
Fig. 3 The oligomer peaks of each single commercial grade PEGs (400 mg L^{-1} for PEG 1000 and 1600 mg L^{-1} for PEG 1500-6000).

Using the four identified peaks as a starting point, the remaining MWs were assigned by adding the 44 g mol^{-1} difference above and below to each oligomer peak (which is the MW associated to the repeating structural unit of CH_2-O-CH_2 in the PEG). The average MW of the commercial grade PEGs (as per Fig. 3) was then used as a confirmation that this process yielded accurate peak MW assignment in the range expected. There was good correspondence between the peak MW expected at these highest peaks within the assignment process indicating that the peak MW assignment was accurate (as

summarised in Table 4). Fig. 4 summarises the identified and assigned MWs of each peak in the PEG mixture. This therefore allows the MW values of any peak associated with any membrane characterised by this method to be directly associated with the MW pattern and elution times in Fig. 4. These peak identities were used to develop calibration curves and using the identified peaks and the concentrations from these calibration curves, filtrations of the feed PEG mixture allowed the rejection of each of the PEG oligomers as a function of the corresponding MW to be determined, which were plotted against MW to give MWCO curves of the membrane used. This process is covered in detail next.

Table 4 Summary of the retention time and peaks with the identified molecular weight

Retention time of the highest peak (min)	5.96±0.02	11.53±0.10	35.29±0.25	48.25±0.077	56.08±0.071	65.88±0.35
Commercial PEGs M_n from suppliers (g mol^{-1})	950-1050	1450-1500	1800-2200	3000	3600-4400	5400-6600
Finalized PEG mixture oligomers' MW (g mol^{-1})	986	1470	2174	3142	4110	6000
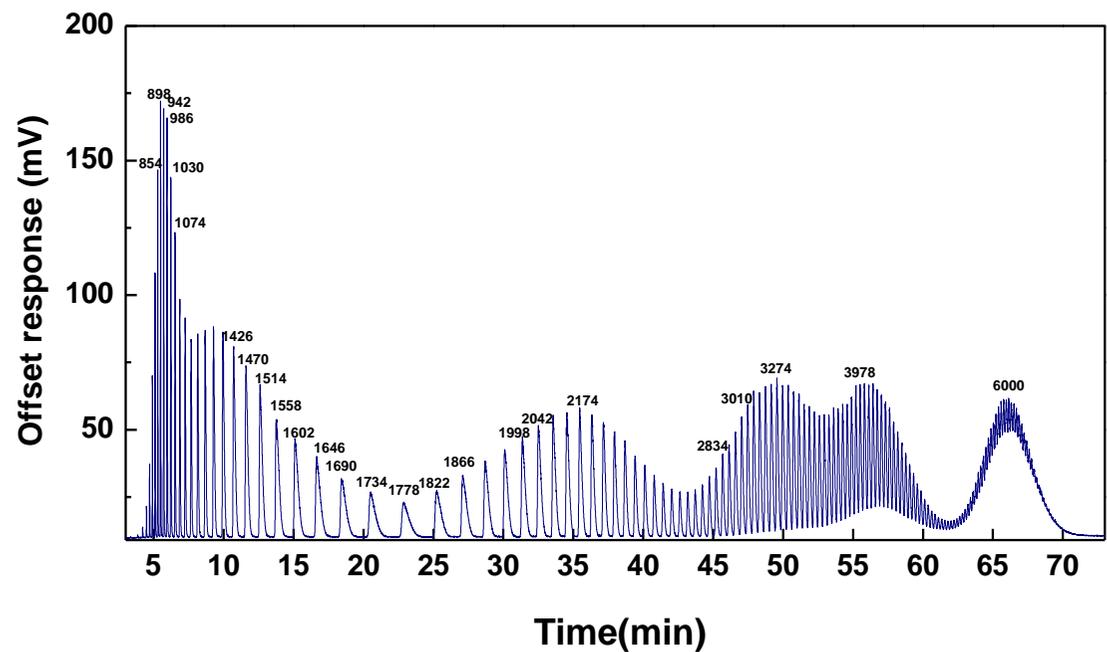
Fig. 4 Identification of individual PEG oligomers mixture from 678 to 6000 g mol^{-1}.

3.3   Obtaining calibration curves

As discussed in Section 3.1, the stock PEG mixture was diluted and analysed to establish a set of external calibrations for each PEG oligomer. One complication identified is shown in Fig. 3, where some peaks from oligomers were present in the oligomer mixture of two different commercial PEGs. These peaks are called "crossover" or "combined" peaks, whose peak area is a combination of the concentration of that oligomer in both adjacent commercial PEGs in the mixture. The "crossover" peaks have been mentioned in a previous study in this research group [1]: the equations and methods to deal with them have been directly adopted from this work (and the equations used in this study are listed in Eq. (1) and (2) in the Supplementary Material). Using all of this information and procedures, a calibration curve for each PEG oligomer was established – detailed information is presented in Fig. S1 in the Supplementary Material.

Generally, a linear response between peak area and concentration is preferable for routine quantitation of concentration [44]. In this study, a linear relationship could be obtained for all the PEG oligomers with correlation coefficients (R^2) of 0.98 and above. However, despite this, a single linear correlation was not sufficient to provide an accurate estimation of PEG oligomer concentration to be used in the rejection calculations needed to form a MWCO curve. This is because the response became slightly non-linear at lower concentrations, especially for the higher MW PEG oligomers. As mentioned, MWCO curves are a plot of rejection (Eq. (1)) vs MW. So, despite a high R^2, extensive testing and comparison of predicted MWCO to expected MWCO of commercial membranes (work not presented) has shown that the difference between the correlations at the lower concentrations (i.e. permeate concentration in Eq. (1)). Higher concentrations (i.e. feed concentration in Eq. (1)) for these PEG oligomers can lead to over or under prediction of the rejections and therefore the MWCO. Therefore, to ensure the rejection of each MW PEG oligomer is calculated accurately, data must be extracted from an equivalent part of the calibration curve which has an equivalent correlation. Therefore for any rejection calculations, it is recommended that the feed and permeate concentration used come from the same section of the calibration curve. To simply doing this, calibration curves are divided into two ranges: the high concentration range and low concentration range (Fig. 5). The range to use in the rejection calculation for a particular membrane is decided by comparing the overall ELSD response of the permeate with that of the feed. If the

membrane rejects much of the PEG mixture, resulting in a permeate ESLD response that is approximately below 1/3 of the feed ELSD response (for ease, this can be qualitatively assessed by comparing the resulting HPLC chromatograms of the ELSD response), it is considered to be part of the low concentration range. In this case, the feed needs to be diluted (and this diluted feed injected into the HPLC for analysis) so that the sample used for the rejection calculation is closer to the permeate concentration to avoid rejection calculation error. Otherwise, if the permeate response is within a similar concentration range to the feed (i.e. in the high concentration range in Fig. 5), the response from both can be used directly without need for feed dilution and rerunning and reanalysis by HPLC.
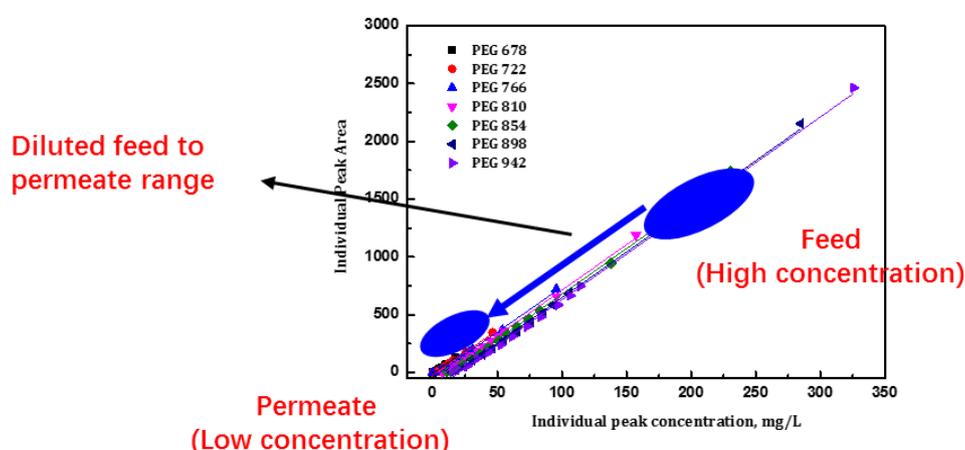
Fig. 5 Example of the two ranges of concentration that need to be considered to minimise rejection calculation error: high concentration range and low concentration range. Feed samples must be diluted to within the permeate concentration range if the ELSD response is approximately more than 2/3 higher than the permeate response.

3.4 Determination of MWCO in commercial membranes

To benchmark the accuracy and appropriateness of the new PEG MWCO method, commercial NF and low UF membranes with manufacturer assessed MWCOs within the applicable range were characterised using the developed PEG method. An example of the HPLC chromatograms of the feed, permeate and retentate samples that are obtained for one of these membranes (a GE Osmonics™ GH) are given in Fig. 6. The resulting HPLC chromatograms from all of the other commercial membranes are given in Figs S2-S7 in the Supplementary Material. For all of the membranes analysed, the ELSD response of the permeate was always lower than that of the feed and the ELSD response for the retentate was always higher than that of the feed, suggesting the membrane separation was as

expected. The permeate ELSD response for the GE Osmonics™ GE and GH, Millipore Ultracel PLAC04310 and PLBC04310 were all lower than 1/3 of the feed ELSD response, therefore for these the feed was diluted into the permeate range and analysed for the rejection calculations for the MWCO curves. The permeate of GE Osmonics™ GK exhibited an ELSD response of more than 1/3 of feed, and so the feed response was directly used for the rejection calculation without dilution.
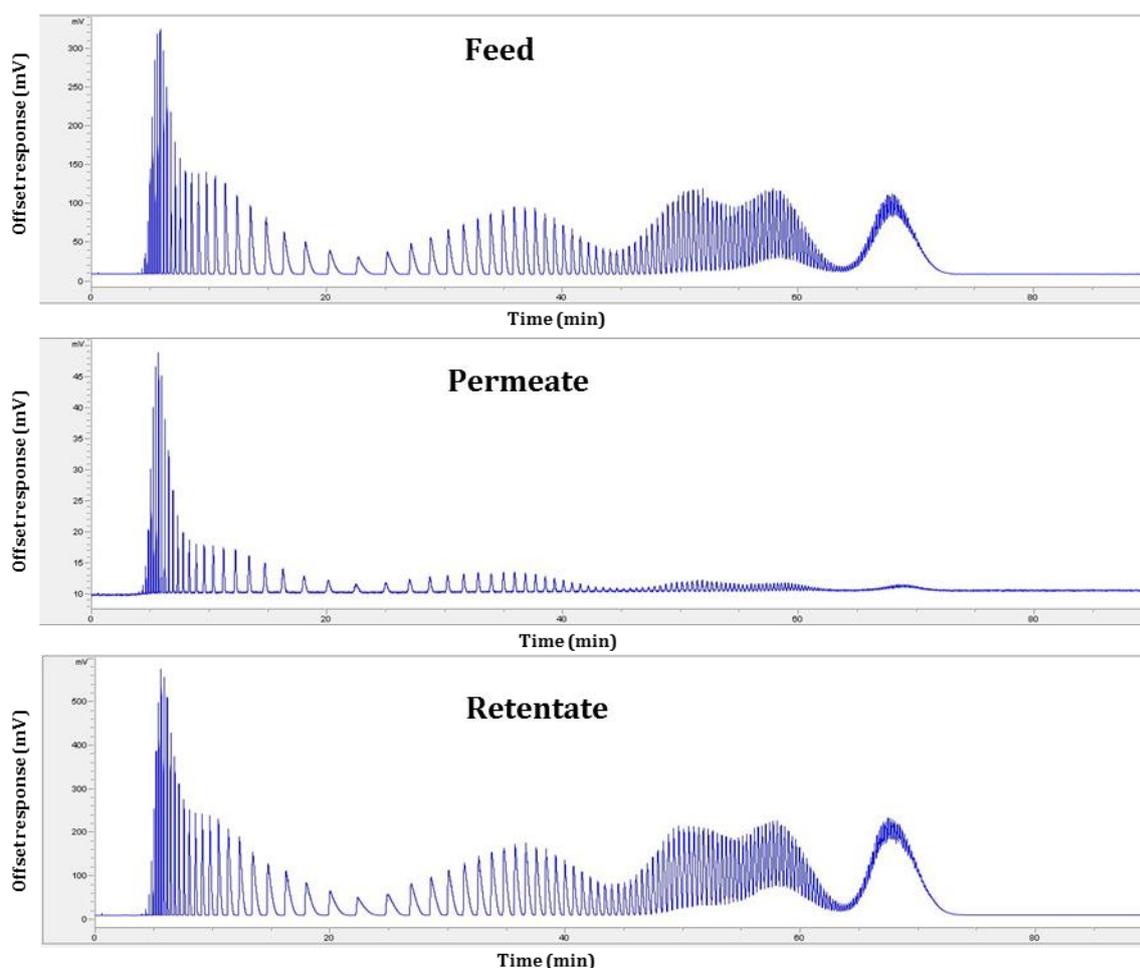
Fig. 6 HPLC chromatograms of feed, permeate and retentate from GE Osmonics™ GH.

The permeance of the membranes with pure water and the PEG mixture (Table 5) differed slightly, which is likely indicative of the difference in viscosity of the solutions.

Rejection of each of the PEG oligomers as a function of the corresponding MW were plotted to give MWCO curves for each of the membranes as shown in Fig. 7. The MWCO from these were compared to the information provided by the manufacturer and in literature (Table 5). This shows that five of the six membranes tested (GE Osmonics™ GE,

GK and GH; Millipore Ultracel PLAC04310 and PLBC04310) gave MWCOs that are in good agreement with the manufacturer and literature values – all of which will have been determined using a different MWCO analysis than this. This indicates that this MWCO method is robust and accurate for most membranes.
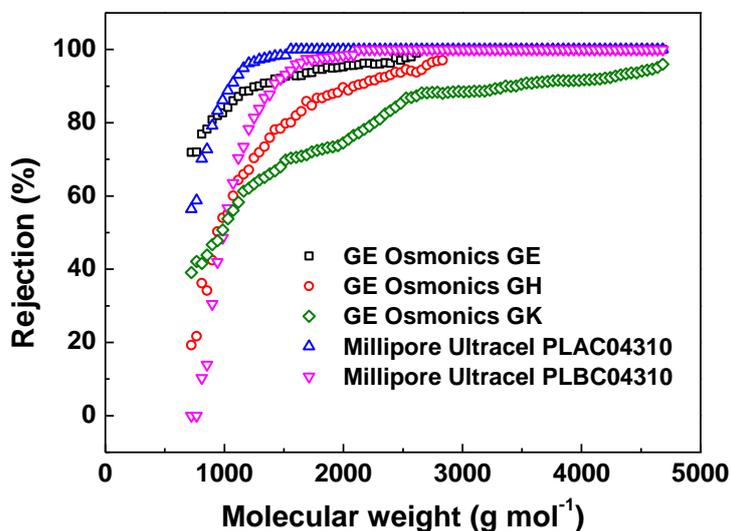
Fig. 7 MWCO curves of commercial membranes using the HPLC-ELSD method.

However, what about the one membrane in Table 5 that deviated? The TriSep UA60 membrane gave a zero ELSD response for all permeate samples, with the retentate giving the strongest ELSD response of the six commercial membranes. This indicates a 100% rejection of all MWs in the PEG mixture, with the TriSep UA60 therefore having a MWCO lower than 678 g mol^{-1} (the lowest MW PEG oligomer in the method). This is unexpected, since the MWCO according to the manufacturer is expected to be 1000-3500 g mol^{-1}. Therefore, Rose Bengal was also used to determine the membrane rejection. This showed a 100% rejection (the permeate was colourless; Fig. S8 in the Supplementary Material). This high rejection confirmed that the MWCO of TriSep UV60 is less than 974 g mol^{-1} (the MW of Rose Bengal) – confirming that the result from the PEG MWCO method is not unreasonable. Based on these two separate and different MWCO tests, it is assumed that the MWCO of the TriSep UA60 stated by the manufacturer is incorrect for the membranes supplied. It is recommended that the manufacturer retest their membrane MWCO, perhaps using the method in this work.

Therefore, overall these results confirm that the newly developed one-filtration PEG method is accurate and comparable to MWCO determined by other methods used by

membrane manufacturers and other researchers. Moreover, this new method gives the widest MWCO range with the highest resolution for aqueous based membranes in a single filtration so far, and so it is recommended that it could be adopted as the new standard MWCO test for NF and low UF membranes for aqueous based separations.

Table 5 Membrane separation properties (Permeance and MWCO) of different commercial membranes obtained using the methods outlined in this paper compared with MWCO from the membrane manufacturers

Membrane type	Water permeance ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)	PEG mixture permeance ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)	Water permeance as supplied by manufacturer ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)	MWCO measured ($g \cdot mol^{-1}$)	Nominal MWCO range ($g \cdot mol^{-1}$)
GE Osmonics™ GE	1.88±0.088	1.08±0.061	1.12	1294±20	1000 [34, 35]
GE Osmonics™ GH	3.22±0.17	1.71±0.060	3.33	1866±373	1000-2500 [30, 34, 36, 37]
GE Osmonics™ GK	9.28±0.99	5.64±0.53	5.66	3956±716	2000-3500 [30, 34, 36, 38]
TriSep UA60	9.35±0.73	5.07±0.38	7.94	<678	1000-3500 [39]
Millipore Ultracel PLAC04310	2.45±0.062	1.98±0.019	---	1030±62	1000 [40]
Millipore Ultracel PLBC04310	6.98±0.70	4.64±0.35	---	1404±31	1000-3000* [41, 42]

* Manufacturer states a MWCO of 3000 but notes that the MWCO could be 2-3 times smaller than the molecular weight of the solute to be retained when using regenerated cellulose.

4   Conclusions

A reliable, cost effective, single filtration method for evaluating the MWCO of aqueous based NF and low MWCO UF membranes has been developed. Intrinsic to this is a new HPLC-ELSD technique that allows resolution of individual PEG oligomers from 678 to 4594 g mol^{-1}. MWCO determination of five commercial membranes from GE Osmonics™ and Millipore showed good agreement with manufacturer and literature values, confirming the accuracy of the method. The MWCO for a TriSep UA60 membrane was lower than that stated by the manufacturer (< 678 g mol^{-1}), however a rejection test with Rose Bengal (MW of 974 g mol^{-1}) indicates that it may be that the MWCO of the supplied membranes is in fact incorrect. It is recommended that the manufacturer retests their membrane MWCO, perhaps using the method in this work.

Consequently, this work is a significant extension to the MWCO method arsenal, with the single filtration MWCO range significantly extended from 678 to 4594 g mol^{-1} with a MW difference of just 44 g mol^{-1} and an additional MW at 6000 g mol^{-1}. This new method therefore gives the widest MWCO range with the highest resolution for aqueous based membranes in a single filtration so far.

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Notes

The authors declare no competing financial interest.

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