



Water-soluble polymers: Emerging contaminants detected, separated and quantified by a novel GPC/MALDI-TOF method[☆]

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ABSTRACT

Water-soluble polymers (WSPs) are additives used as thickeners, stabilisers and flocculants in industry and in household products, including personal care products. Given their widespread use, it is likely WSPs enter the environment, particularly through wastewaters. This is of concern as there is little ecotoxicological research on their fate and behaviour once in the environment, which means their risk to aquatic life is not understood. The lack of suitable analytical techniques to detect, characterise and quantify WSPs hinders research on the potential impact of these polymers. A novel method has been developed that identifies polymers within a sample and separates them using gel-permeation chromatography (GPC). This is coupled with matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF MS), to quantify the polymer fractions using molecular weight information. This process has been carried out on a range of aqueous media. Polyethylene glycol (PEG) ingredients were successfully separated from non-polymeric material in a commercial shaving gel personal care product (PCP), before being quantified at 1.62 wt%. This method was applied to a spiked wastewater influent sample to demonstrate the extraction and separation of PEG from organic constituents such as dissolved organic matter (DOM). This highlighted the additional challenges of analysing WSPs in the environment, as factors such as sorption and biodegradation affected the total recovery of PEG, with an extraction efficiency of 53%. Overall, this method was applied for the extraction of PEG from a PCP with accurate quantification, before a proof-of-concept extraction from wastewater demonstrated the difficulties associated with WSP analysis in environmental samples. This method provides opportunities to use tandem GPC/MALDI-TOF MS to quantify WSPs in a broad array of environmental samples. Additional studies could include its application to wastewater or freshwater monitoring.

1. Introduction

Over the last decade, micro and nanoplastics containing synthetic polymers have moved to the forefront of polymer research. Their small sizes (<5 mm and <1 µm for microplastics and nanoplastics respectively) have been identified as a key factor in their translocation into a range of terrestrial and marine environments, including remote polar and mountainous regions (Jiang et al., 2019; Yin et al., 2021). Recent research has highlighted adverse ecotoxicological effects caused by the

persistence of these polymers in the environment; consequently the European Chemicals Agency (ECHA) proposed the restriction of intentionally added microplastics (between 5 and 15 mm) that may result in environmental release in 2017, reducing emissions by approximately 500 thousand tonnes over the next 20 years (ECHA, 2019; Wang et al., 2019).

While plastics are now recognised as a significant threat to the environment, most of this research implies that only insoluble polymers are a cause for concern (Arp and Knutsen, 2020). Water-soluble

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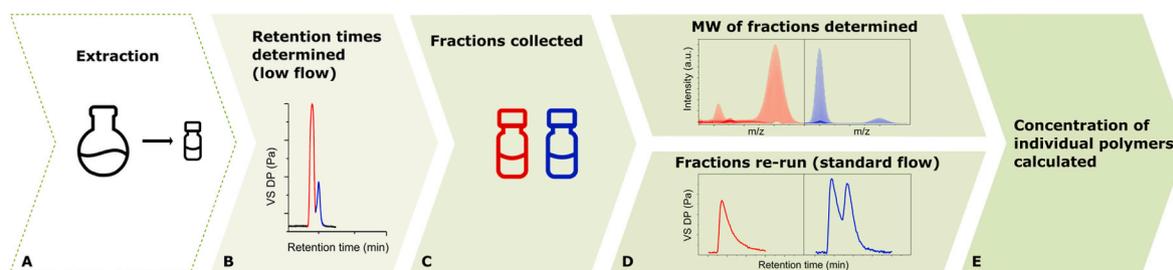


Fig. 1. A schematic outlining the main steps involved in the GPC/MALDI-TOF method developed in this paper.

polymers (WSPs) are polymers “that dissolve, disperse, or swell in water and thus modify the physical properties of aqueous systems” (Kadajji and Betageri, 2011). The applications of WSPs are vast; for example, polyacrylamides (PAMs) are commonly used as flocculants in wastewater treatment and in the oil recovery industry while polyacrylic acids (PAAs) are used as cement modifiers. Polymers such as polyethylene glycol (PEG), polypropylene glycol (PPG) and polyvinylpyrrolidone (PVP) are used in pharmaceuticals and personal care products (PPCPs) as emulsion stabilisers and thickeners (Afolabi et al., 2019; Badawi et al., 2023; Rozman and Kalcikova, 2021; Tarannum et al., 2020; Umoren et al., 2006). However, their use spans many more industrial and household industries and products, and their use in society is ubiquitous. Their solubility is governed by factors such as molecular weight, monomer combination and chemical functionality, but there is no defined size-scale between soluble and insoluble (Arp and Knutsen, 2020). Therefore, WSPs can have a molecular weight as low as a few hundred to hundreds of thousands of Daltons. As well as their large (molecular) size range, WSP formulations tend to have a broad molecular weight range within a sample, defined as polydisperse, which can make their analysis through methods like size-exclusion chromatography (SEC) difficult (Mairinger et al., 2021).

Confusion over polymer classes and ambiguity in the terminology used in both research and legislation can exclude soluble polymers from regulation. Hartmann et al. have developed a physicochemical framework to categorise plastic debris; while advancing the current size-based framework, it excludes WSPs by virtue of their solubility (Hartmann et al., 2019).

Despite insoluble and soluble polymers having many similarities, their behaviour and impact in the environment cannot be considered the same. Insoluble polymers, such as microplastics, can affect ecosystems through physical processes such as changing the density and porosity of soil or biofilm formation on plastic surfaces, increasing pollution sorption onto said surfaces (Ho et al., 2020; Kumar et al., 2023). On the other hand, the preliminary studies into the impact of WSPs suggest that these polymers can impact the environment at the molecular level, including altering the viscosity of solutions, increasing soil water retention and flocculating environmental matter (Bolto and Gregory, 2007; Rozman and Kalcikova, 2021; Xiong et al., 2018).

Only very recently have broad reviews, lab-based studies on toxicity and the first quantitative methods for WSPs been published, highlighting the detrimental chronic effects these polymers pose to the growth, development and reproduction of aquatic species (Duis et al., 2021; Huppertsberg et al., 2020; Kadajji and Betageri, 2011; Lee et al., 2014; Mondellini et al., 2022; Patil and Ferritto, 2012; Pauelsen et al., 2023; Sverdrup et al., 2001; Wang et al., 2023). Therefore, WSPs are currently not regulated under the registration, evaluation, authorisation and restriction of chemicals (REACH) and consequently are not currently monitored as an environmental pollutant (Arp and Knutsen, 2020; ECHA, 2017; Huppertsberg et al., 2020). This lack of research leading to insufficient legislation leaves a comparative gap in WSP research compared to other polymers and plastics, which have garnered greater attention in both regulatory and research spheres.

A significant hindrance to advancing the understanding of WSP

pollution is the lack of suitable analytical techniques to analyse polymers in the environment. The principal methods to investigate polymer characteristics are gel-permeation chromatography (GPC) and matrix-assisted laser desorption/ionisation-time-of-flight mass spectrometry (MALDI-TOF MS). GPC, a type of SEC, separates polymers by their hydrodynamic radii, which has been shown to be directly proportional to polymer chain length (Yau et al., 1979). After calibration, accurate concentrations are used to determine the molecular weight of the polymer in solution, with this method having been applied to WSPs in a range of solvents (Baines et al., 1996; Mineo et al., 2002; Tamani et al., 2020; Tulu et al., 2009).

MALDI-TOF MS was first used in 1988 for the analysis of polymers and proteins (Tanaka et al., 1988). Since then, MALDI methodology has expanded and predominantly consists of a polymer solution, an organic matrix and an ionisation reagent. The laser is absorbed by the matrix before this energy causes cations from the ionisation source to transfer to the analyte molecules, enabling their detection (Batoy et al., 2008). This soft ionisation process has been adapted with different matrices and MALDI “recipes” to enhance the analysis and molecular weight determination of peptides, proteins and polymers (Brandt et al., 2010). More recently MALDI-TOF MS has been used in the analysis of environmental samples and WSPs (Altuntas et al., 2012; Danis et al., 1992; Loiseau et al., 2003; Malvagna et al., 2002; Nunes et al., 2020; Rivas et al., 2016; Trimpin et al., 2001; Zalewska et al., 2003).

Using both GPC and MALDI-TOF analytical methods to characterise and quantify WSPs in the environment presents numerous challenges. The introduction of solid and dissolved organic matter (DOM) impacts the sorption and degradation of polymers (Bernhard et al., 2008; Cumming et al., 2011b; Eubeler et al., 2010). Accurate molecular weights can be determined from GPC but only if the concentration of the sample is known, while MALDI-TOF MS is not quantitative, despite having a lower detection limit than GPC.

The coupling of SEC instrumentation to MALDI-TOF MS was first proposed in 1995 by Montaudo et al. for the fractionation of polydisperse polymer samples and the accurate molecular weight determination of these fractions (Montaudo et al., 1995). Since then it has been applied to polydisperse polymers and copolymers, but only to characterise known polymer samples (Adamus et al., 2006; Deery et al., 2001; Hanton and Liu, 2000; Jayakannan et al., 2002; Kassis et al., 1997; Kona et al., 2005; Montaudo et al., 1997; Montaudo and Montaudo, 1999; Montaudo et al., 1998a, b; Murgasova and Hercules, 2002; Nielsen and Malucha, 1997; Salhi et al., 2005; Sato et al., 2003). To date and to the best of our knowledge, this method has not been applied to calculate fraction sample concentrations from mass spectral molecular weights.

With a focus on environmental pollution, this method could potentially be used to identify individual polymer identities and calculate concentrations in freshwater, as recently demonstrated by Pauelsen et al. using an alternative method (Pauelsen et al., 2023). This pioneering work, along with the European Commission’s current review on grouping polymer classes for registration under REACH, emphasises the need to advance analytical methodology and address the growing question around WSP pollution (European Commission, 2022). In this paper, a GPC/MALDI-TOF method is applied with the aim of separating,

determining the molecular weight of and calculating the concentration of a range of polyethylene glycol (PEG) samples, ranging in complexity and environmental relevance, from standard samples to personal care products (PCPs) and wastewater samples. It is expected that using methods specifically designed for polymer analysis will facilitate a broader application to the full range of polymer identities and molecular weights found in freshwater systems. Not only will this research improve fundamental knowledge of WSP pollution, but understanding the harm products such as PCPs pose to the environment could have wide-reaching societal implications.

2. Materials and methods

The initial aim of the study was to couple GPC and MALDI-TOF to separate polymers in a range of solutions and calculate their molecular weights, which can in turn be used to calculate their concentration and molecular identities. This method is termed GPC/MALDI-TOF. This overview is laid out in Fig. 1 (steps B-E). In step B, the retention times of the polymers in the sample was determined using a low flow rate, which enabled the separation of polymers within the sample. This step was repeated, with eluent fractions collected from the GPC corresponding to these retention times, plus the time delay between detector and solvent outlet (step C). Each fraction was subjected to MALDI-TOF MS to calculate the molecular weight of the polymer in the fraction (step D). Simultaneously, the fractions were analysed on the GPC at the standard flow rate, which corresponded to the calibration curve of the instrument. These GPC traces were then analysed, and the fraction concentration manipulated in the software until the number average molecular weight (M_n) reading was the same as the M_n calculated from the MALDI-TOF spectra (step E). This approach was used to identify the inherent error associated with the method, which in turn determined its accuracy.

Alongside GPC/MALDI-TOF, which can be applied to pure samples, an additional extraction step can be performed for the analysis of aqueous samples, prior to the aforementioned steps. This method is termed extraction/GPC/MALDI-TOF (steps A-E). An extraction step is necessary for environmental samples, where water and solid impurities must be removed before analysis (Step A). This step introduces further error into the method, as there will be inevitable loss of polymer through physicochemical processes, such as sorption and biodegradation, and methodical processes such as filtration and transferal.

The identification of errors in both the core and pre-processing method is essential if the accuracy and applicability of the method is to be tested. Alongside this, errors in environmental chemistry must be assigned for environmental modelling and prediction of analyte concentration. Therefore, applying the GPC/MALDI-TOF method to a range of samples, increasing in complexity, can ascertain if this process can be used to separate and quantify WSPs, while identifying and assigning the intrinsic errors in environmental analysis.

2.1. Materials

Polyethylene glycol (PEG) standards ($M_n = 2000, 6000$) were supplied by Sigma-Aldrich (Gillingham, UK). The shaving gel sample was purchased from a highstreet retailer with no further modification. Autoclaved raw wastewater influent was obtained from a range of wastewater treatment plants throughout the south and west UK. The samples used for this study were amalgamated from multiple sites. Parameters for wastewater collected from these sites can be found in the Supplementary Information (SI1.1). Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyldiene]malononitrile (DCTB) MALDI matrix and sodium acetate were purchased from Sigma-Aldrich. GPC and HPLC grade THF were purchased from Fisher Scientific (Loughborough, UK).

2.2. Methods

2.2.1. GPC sample preparation

The PEG 2000 and 6000 standards were each dissolved in HPLC grade THF (30 mg mL⁻¹ each). 1 mL of PEG 2000 and 1.5 mL of PEG 6000 were combined to give the final concentrated solution. This solution was then filtered through a 1 mL glass syringe and 0.2 μm PTFE filter.

The shaving gel sample was dissolved in THF (100 mg mL⁻¹) and filtered using the same methodology as the standards.

For the distilled water spiking, the PEG 2000 and 6000 standards were made up in distilled water (30 mg mL⁻¹ each). 1 mL of PEG 2000 and 1.5 mL of PEG 6000 were combined to give the final solution which was added directly to 1 L of distilled water. The water was removed from the sample via rotary evaporation. The solid residue was dissolved in THF (100 mL) and heated to reflux. The solids were then manually agitated before again heating to reflux. The solids were filtered out of solution using filter paper and the sample evaporated to dryness via rotary evaporation before being dissolved in THF (2 mL). The sample was filtered following the same methodology as the above standards and shaving gel sample.

The wastewater spiking followed the same protocol as the distilled water spiking, with the standards added to 1 L of autoclaved wastewater influent.

2.2.2. MALDI-TOF sample preparation

Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldiene]malononitrile (DCTB) (20 mg mL⁻¹ in THF) was used as the matrix. Sodium acetate (NaOAc) (50 mg mL⁻¹ in THF) was used as the cationisation reagent. Solutions of matrix, sample and cationisation reagent were mixed in a 5:15:1 vol ratio and approximately 1 μL of this solution was spotted on the MALDI plate and dried at room temperature in a fumehood.

2.2.3. GPC instrumentation, calibration and detector correction

GPC analysis was carried out in THF with two PLgel 5 μm MIXED-D columns (300 × 7.5 mm) in series using an Agilent InfinityLab LC series 1260 Infinity Quaternary system connected to an Agilent 1260 Infinity GPC/SEC Multi Detector Suite (MDS). The MDS comprised of a dual angle light scattering detector, refractive index detector and viscometer in order.

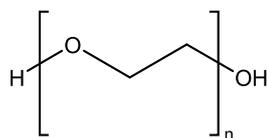
The MDS triple detectors were aligned using a polystyrene standard (100 μL, 1 mg mL⁻¹, $M_n = 87,950$, $dn/dc = 0.185$ g mL⁻¹) in the Agilent GPC/SEC software. The detectors were calibrated using Agilent Polystyrene Medium EasiVials (100 μL, 2 mg mL⁻¹). Both calibration steps were performed at a flow rate of 1 mL min⁻¹.

The delay between the viscometry detector and the elution of solvent from the instrument was determined using the PEG 2000 standard (3 mg mL⁻¹). The sample was injected into the instrument at 0.1 mL min⁻¹ for 400 min and the retention time of the peak recorded (160–176 min). This process was repeated with 53 fractions collected every minute between 150 and 202 min. These fractions were evaporated to dryness and redissolved in THF (1 mL). MALDI-TOF mass spectra of each fraction were then recorded to identify which fractions contained PEG 2000. PEG was identified as eluting from the instrument at 177 min which equated to a 17-min delay between viscometer and the elution of solvent from the instrument. This time delay was added to each sample retention time throughout the study.

2.2.4. Molecular weight determination of the standards

The number average molecular weight (M_n) of the standards was determined using MALDI-TOF mass spectrometry. M_n is calculated using Equation 1, where N_i is the number of chains of a particular molecular weight and M_i is the molecular weight of those chains.

The molecular weights of the PEG 2000 and PEG 6000 standards were determined to be 2028 and 5445 Da respectively. Equation 1:



Repeat unit molecular weight: 44.05

Fig. 2. The chemical structure poly(ethylene glycol) (PEG).

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

2.2.5. GPC analysis and fractionation

Following the preparation of the samples, each sample (100 μL) was injected into the instrument at a flow rate of 0.1 mL min^{-1} over 400 min. Sample differential pressure viscometry (DP VS) peaks were identified the sample (100 μL) was injected again at 0.1 mL min^{-1} over 400 min with fractions collected from the instrument waste stream corresponding to the VS DP retention times. Fractions were blown to dryness under argon and dissolved in THF (0.75 mL). The fractions (100 μL) were then injected at a flow rate of 1 mL min^{-1} over 40 min.

2.2.6. MALDI-TOF analysis

MALDI-TOF mass spectra were run in positive ion mode using a Bruker Autoflex Speed mass spectrometer (Bremen, Germany) equipped with a 340 nm nitrogen laser. The spectra were acquired in flexControl 3.4 in linear mode and analysed in flexAnalysis 3.4. All spectra were baseline corrected.

3. Results and discussion

3.1. GPC/MALDI-TOF method

3.1.1. Fractionation and concentration determination

The accuracy of the extraction-free GPC/MALDI-TOF method in determining polymer concentration was established using PEG 2000 and PEG 6000 standards. By applying the method to polymer standards of known concentrations, the error in the instrument and sample preparation can be calculated.

The standard sample was initially analysed on the GPC instrument at 0.1 mL min^{-1} to allow for the greatest possible separation of the polymer standards, while not falling below the minimum operational flow for the GPC column. This produced a differential pressure viscometry trace with two major peaks, followed by a third low intensity peak that can be assigned to low molecular weight matter from the THF solvent (SI2.1, SI2.2, SI3.1).

MALDI-TOF mass spectra confirmed the presence of the standards in the GPC trace. The spectra showed two molecular weight distributions around 2000 and 6000 Da (SI3.2). The peaks contain ions with a mass difference of 44 Da, which can be assigned to the OCH_2CH_2 repeat unit of PEG (Fig. 2).

The standard sample was re-run on the GPC instrument at 0.1 mL min^{-1} and two fractions collected, corresponding to the retention times of the two peaks in the initial GPC trace. These fractions were then run at 1 mL min^{-1} to enable the PEG standards to be eluted at a retention time corresponding to the calibration curve of the instrument. As well as the GPC viscometry trace, MALDI-TOF mass spectra were recorded for each fraction (Fig. 3). The average retention times for both fractions are listed in SI4.1.

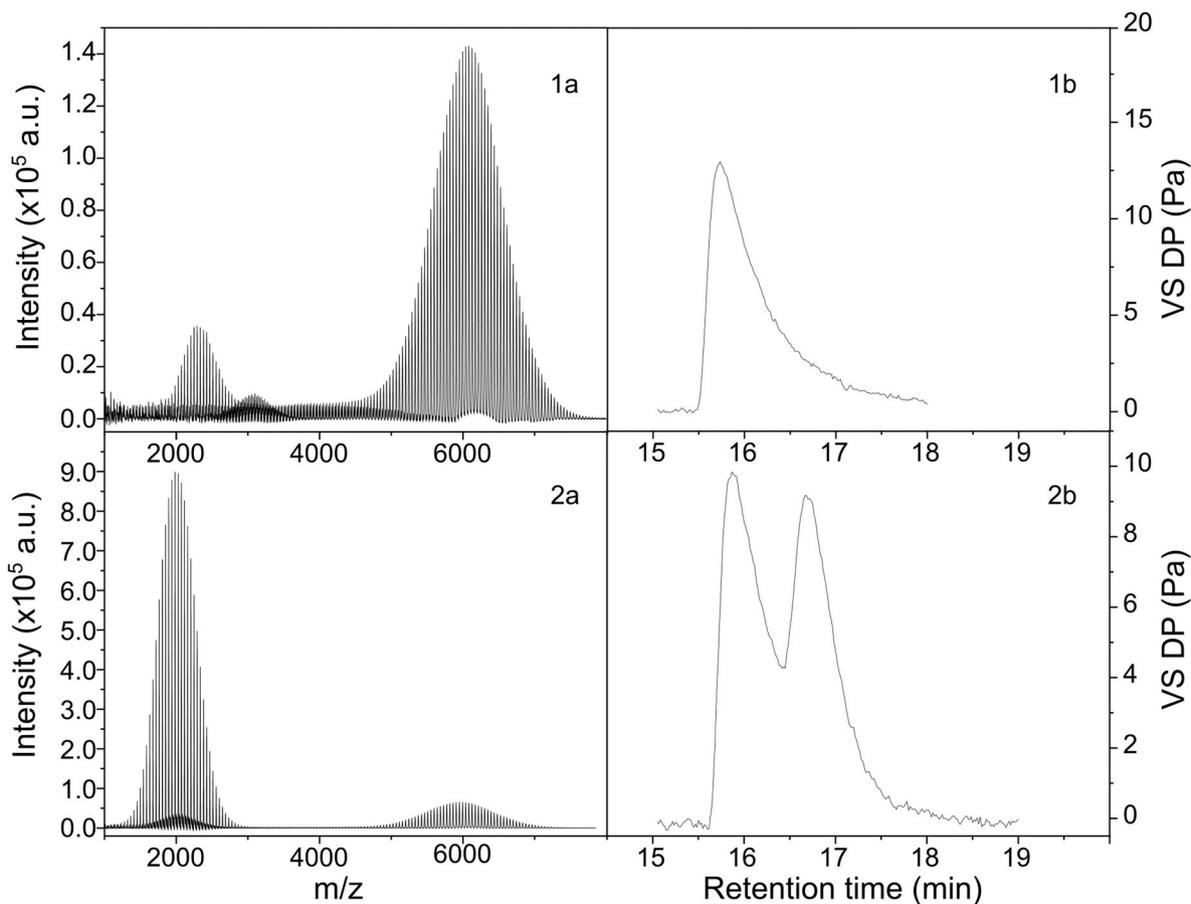


Fig. 3. A MALDI-TOF spectrum of the PEG sample fractions collected from the GPC instrument 1a) Fraction 1 2a) Fraction 2 A GPC chromatogram of the PEG sample fractions collected at 0.1 mL min^{-1} and re-run at 1 mL min^{-1} 1b) Fraction 1 2b) Fraction 2.

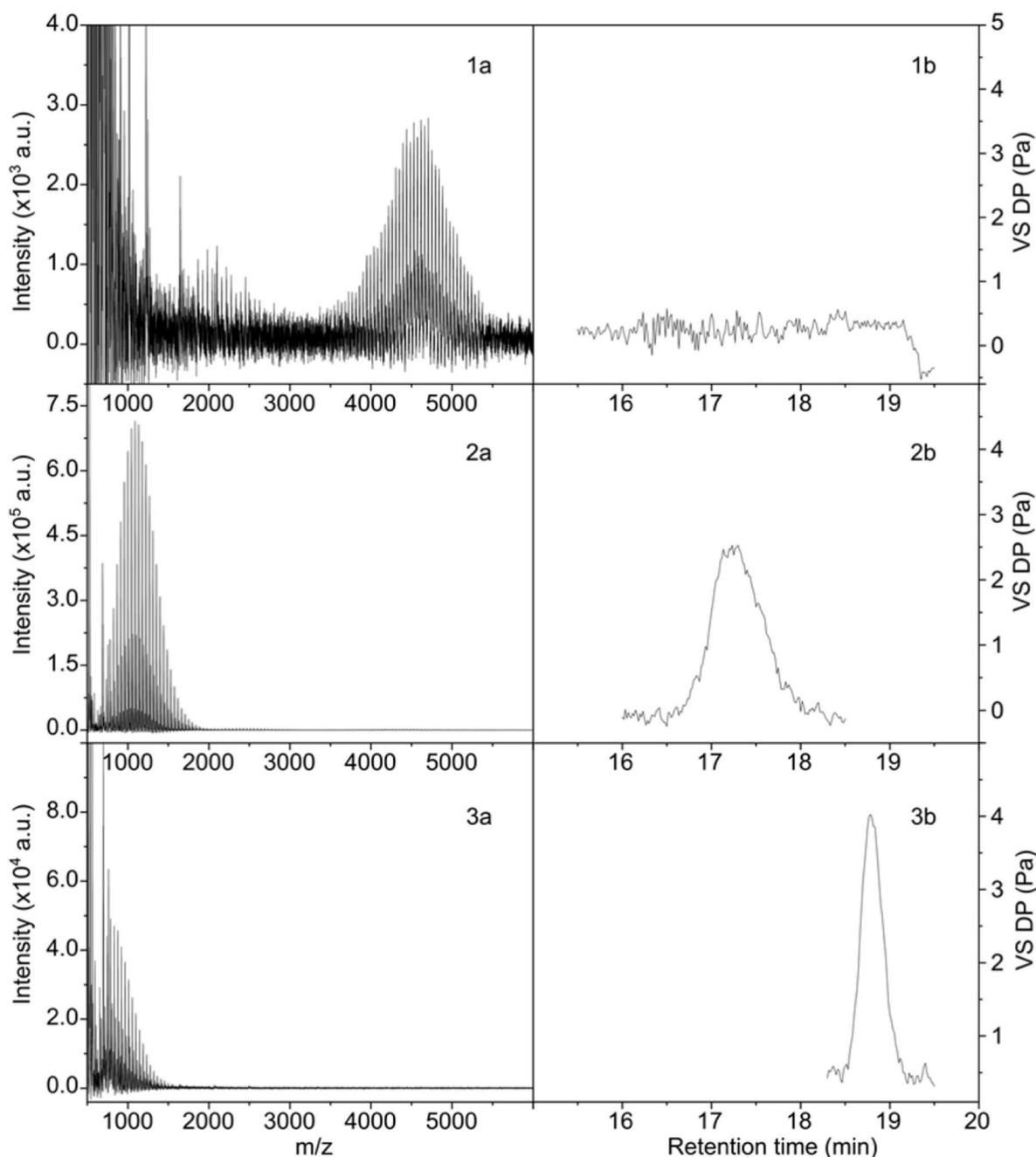


Fig. 4. A MALDI-TOF spectrum of the shaving gel sample fractions collected from the GPC instrument 1a) Fraction 1 2a) Fraction 2 3a) Fraction 3. A GPC chromatogram of the shaving gel sample fractions collected at 0.1 mL min^{-1} and re-run at 1 mL min^{-1} 1b) Fraction 1 2b) Fraction 2 3b) Fraction 3.

The MALDI-TOF spectra demonstrate Fractions 1 and 2 contain predominantly PEG 6000 and PEG 2000 respectively, with trace amounts of the other polymer in each sample. The GPCs of the fractions reflect this, with a broad peak in fraction 1 indicating some PEG 2000 remains in the sample, while fraction 2 contains two peaks, similarly suggesting PEG 6000 residue in the sample.

The GPC instrument software uses inputted concentrations to give a molecular weight output. Therefore, the concentration of the fractions was calculated by varying concentration until the correct molecular weight was reached (SI5.1).

The calculated M_n for the fractions reflects the residue of each polymer remaining in each sample, with fraction 1 having a lower molecular weight and fraction two having a higher molecular weight than expected if complete separation had occurred.

The total concentration of PEG in the sample was calculated to be

$2.69 \pm 0.27 \text{ mg mL}^{-1}$; since 3 mg mL^{-1} was used in the experiment, this gives an error margin of 10% in this case.

3.1.2. Application to a personal care product (PCP)

Following on from the concentration determination in a standard sample, the GPC/MALDI-TOF method was then tested on a commercial sample, representing a class of substances likely to enter freshwater through wastewater treatment. A shaving gel PCP was selected that contained two PEG ingredients to ensure viable separation of these polymers. While the shaving gel sample contains PEG ingredients, the concentration and molecular identity of these ingredients is unknown. The same procedure was applied to the shaving gel as was applied to the standard sample, discussed above.

The sample was run on the GPC at 0.1 mL min^{-1} to identify peak retention times, with a MALDI-TOF mass spectrum confirming the

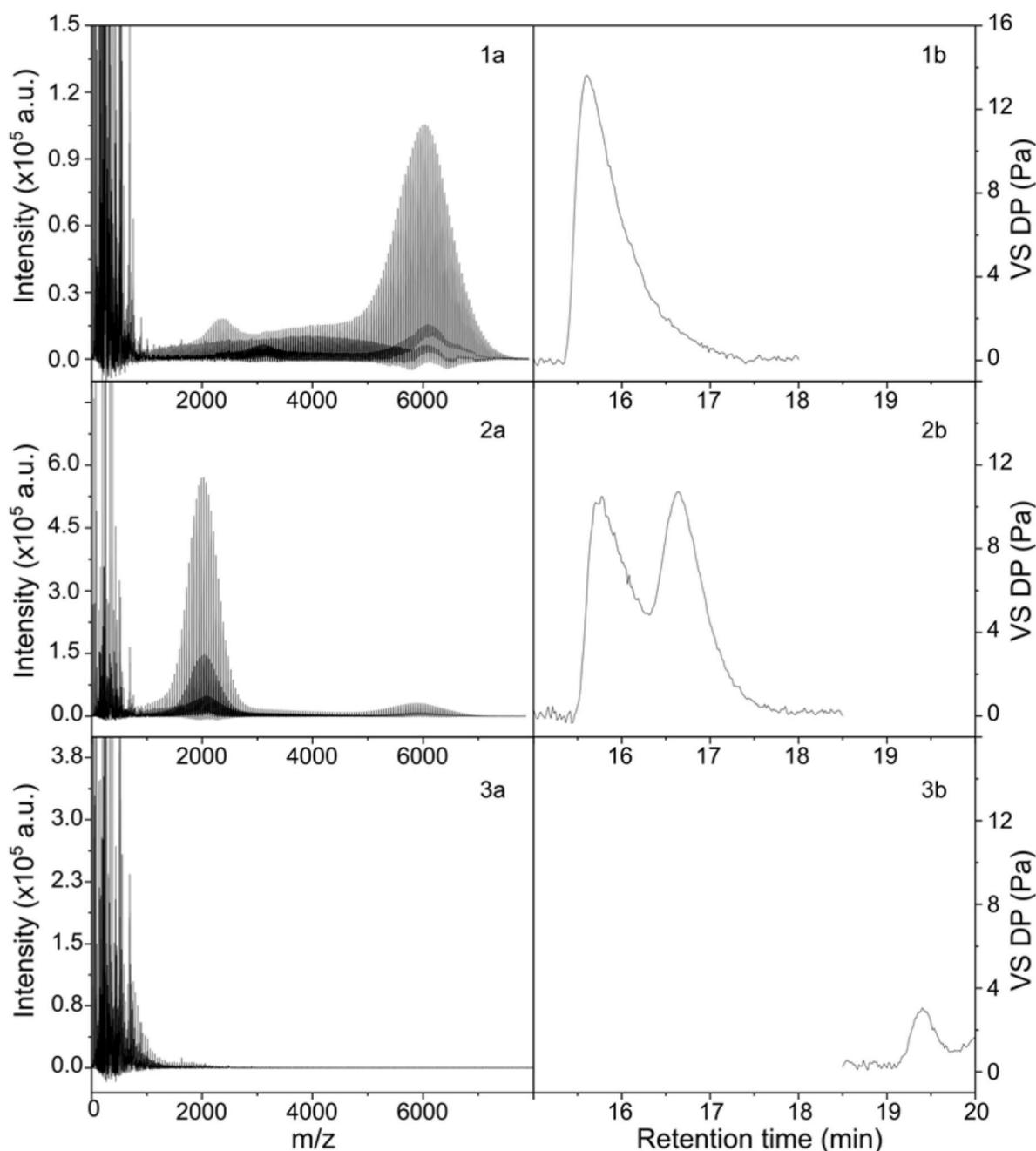


Fig. 5. A MALDI-TOF spectrum of PEG fractions extracted from distilled water collected from the GPC instrument 1a) Fraction 1 2a) Fraction 2 3a) Fraction 3 A GPC chromatogram of the PEG fractions extracted from distilled water collected at 0.1 mL min^{-1} and re-run at 1 mL min^{-1} 1b) Fraction 1 2b) Fraction 2 3b) Fraction 3.

presence of the PEG ingredients (SI2.3, SI3.3).

The GPC viscometry trace for the shaving gel PCP contains 3 main peaks in the chromatogram, with two smaller shoulder peaks also present. The MALDI-TOF mass spectrum confirms the presence of PEG in the sample, with multiple high intensity polymer series around 1000 Da containing ions with 44 Da spacings. Lower intensity series of PEG were also observed at 2500 and 4500 Da.

The 5 fractions were collected and analysed at 1 mL min^{-1} ; retention times are listed in SI4.2. MALDI-TOF spectra were used to identify the PEG-containing fractions, from which it is concluded that fractions 1, 2 and 3 contain PEG, while fractions 4 and 5 only contain low molecular weight non-polymeric material (Fig. 4). Fraction 1 did not contain a high enough concentration of PEG to obtain a GPC trace when re-analysed and could therefore not be further processed to calculate concentration. Consequently, it is expected the GPC/MALDI-TOF method will

underestimate the quantity of PEG in the personal care product.

Using the molecular weight of fractions 2 and 3, the average concentration of PEG was 1.62 mg mL^{-1} per 100 mg of shaving gel (SI5.2).

3.1.3. Effectiveness of the method

The initial aim of the study was to prove the effectiveness and accuracy of the GPC/MALDI-TOF method in detecting WSPs without any complicating factors that beset environmental samples. The separation of the PEG standards of known concentration was successful, with only trace amounts of each polymer contaminating the partner polymer after separation. Numerous characteristics define the ability of polymers to be separated in solution; for example, PEG 2000 and 6000 correspond to the number average molecular weights of the polymers, however these have similar retention times, thus reducing the effectiveness of their separation. The greater polydispersity of the PEG 6000 standard,

coupled with narrow region between the two molecular weight distributions, likely hinders their complete separation in solution and renders a degree of cross-contamination in the GPC/MALDI-TOF procedure inevitable. Nevertheless, cross-contamination was minimal and the error in the total calculated concentration was commensurate with the expected error for GPC, which has been reported as 10–20% (Voorter et al., 2022). Overall, our data suggest that the method is viable as an analytical tool.

While GPC/MALDI-TOF allowed us to separate two PEG polymers with high accuracy, this method will give the greatest impact in environmental analysis if it can be used for the separation of more complex real-world samples with multiple polymer and non-polymer components. By analysing a shaving gel PCP under ideal laboratory conditions, a measured step is taken towards environmental analysis. As well as being more complex analytically, PCPs have been reported as one of the major WSP-containing groups expected to enter the environment, likely through wastewater treatment, primarily due their high volume and widespread use in household products (Cumming et al., 2011a; Duis et al., 2021; Rozman and Kalcikova, 2021). Despite the challenges presented by a non-uniform sample, three polymeric fractions were separated from two non-polymeric fractions, demonstrating that non-polymeric components can be removed to enable WSP analysis. This is significant for future applications of the method, spanning household, industrial and agricultural products. These formulations are poorly characterised which means further analysis into WSPs within the product and their potential environmental impact cannot be explored. The ability to isolate these polymers and not only identify the type of polymer but the molecular weight and concentration would be a huge step towards WSP regulation.

The inability to determine the concentration of the first fraction due to detection limits highlights a limitation of the method, but this problem is necessarily associated with low concentration components and is not expected to add substantially to the error margins of the technique. The polymer concentration of 1.62 wt% is consistent with several commercial shaving gel formulations, which contain WSPs between 1 and 3 %w/w, demonstrating that not only is the GPC/MALDI-TOF method accurate, but can be used to separate and quantify the polymeric material in a highstreet PCP, opening up the avenue of its use on environmental samples.

3.2. Extraction/GPC/MALDI-TOF method

3.2.1. Extraction, fractionation and concentration determination

To verify the effect of adding an extraction step to the analysis of WSPs, PEG 2000 and 6000 were extracted from distilled water before being analysed in the same way as in Section 4.1. The chromatogram of the extract contains both PEG standards and a small amount of low molecular weight matter, likely residual material from the water (SI2.4). This is supported by the MALDI-TOF spectrum of the extracted sample, which has a similar appearance to the non-extracted PEG spectrum in Section 4.1, with polymer distributions at 2000 and 6000 Da (SI3.4).

The two fractions were collected and analysed by GPC at 1 mL min^{-1} , with retention times for these fractions listed in SI4.3. The first fraction collected contains predominantly PEG 6000, with the second fraction containing PEG 2000 with traces of PEG 6000, as supported by the chromatogram trace of this fraction containing two peaks. The third fraction, interestingly, contains low molecular weight PEG at around 750 Da, which could indicate low levels of degradation, most likely as a result of biodegradation (Section 4.2.2) (Fig. 5). An accurate concentration of this third fraction was not able to be determined from the GPC data, which suggests this low molecular weight PEG is present in only trace amounts.

The concentration determined in the initial two extract fractions concludes that 73% of the spiked polymer was extracted from the distilled water and quantified (SI5.3). This supports our hypothesis that increased error is inherent in the extraction/GPC/MALDI-TOF method.

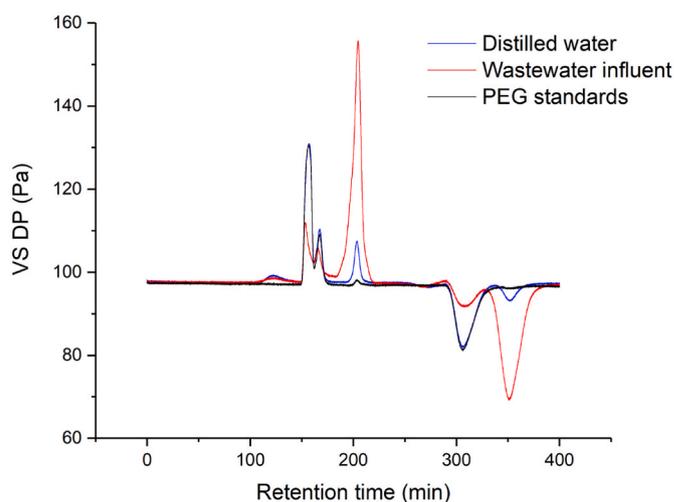


Fig. 6. A GPC chromatogram differential pressure viscometry trace of PEG 2000 and PEG 6000 directly dissolved in THF and the same standards extracted from both distilled water and wastewater influent. The baseline of the wastewater influent and PEG standards trace have been corrected to the distilled water trace.

3.2.2. Application of method to wastewater

Having validated the method on distilled water, the method was applied to a wastewater sample spiked with PEG standards as a pseudo-environmental sample. A blank wastewater sample was also analysed by GPC and MALDI-TOF MS to confirm the chromatograms and spectra analysed are from the spiked polymers (SI2.6, SI3.6).

The extracted sample was analysed by GPC at 0.1 mL min^{-1} ; the chromatogram contained 2 PEG peaks and a low molecular-weight peak, similarly to the distilled water extract. This third peak was at a much greater intensity than the PEG peaks, which is to be expected as this peak incorporates the dissolved organic matter and other low molecular weight material present in the sample (SI2.5). The MALDI-TOF spectrum also confirmed both polymers were present in the sample, however, degraded PEG at a lower molecular weight was also present in the sample, suggesting the introduction of a medium with the potential for bacterial growth may have impacted the polymer standards (SI3.5) (Bernhard et al., 2008; Eubeler et al., 2010; Huang et al., 2005; Pietrelli et al., 2021; Rozman and Kalcikova, 2021).

To investigate this degradation further, the chromatograms for the PEG standards, the distilled water extracts and the wastewater extracts were overlaid for comparison (Fig. 6).

The GPC trace for the PEG standards and distilled water extract are similar, with nearly identical PEG peaks. The only noticeable difference is the greater low molecular weight peak at an increased retention time in the distilled water chromatogram, indicative of residual matter from the water. The wastewater extract chromatogram has noticeably reduced PEG standard peaks, with the second peak broadly tailing into the low molecular weight peak, which is at a much greater intensity than the other two samples (Fig. 6). This information, alongside the MALDI-TOF spectrum of the wastewater extract, supports the biodegradation of PEG within the sample, with no clear definition in the spectrum between each standard, as well as lower molecular weight PEG trailing from the PEG 2000 standard.

The 3 fractions were collected and re-analysed by GPC at 1 mL min^{-1} , with retention times listed in SI4.4 (Fig. 7). Further evidence of biodegradation was present in these fractions, with each fraction containing broad, polydisperse PEG distributions.

The molecular weight and concentration of PEG in the extracted wastewater sample is summarised in SI5.4. PEG 6000 and 2000 are still predominant in the first two fractions, despite the evident degradation, with fraction 3 containing PEG at a much lower molecular weight, likely

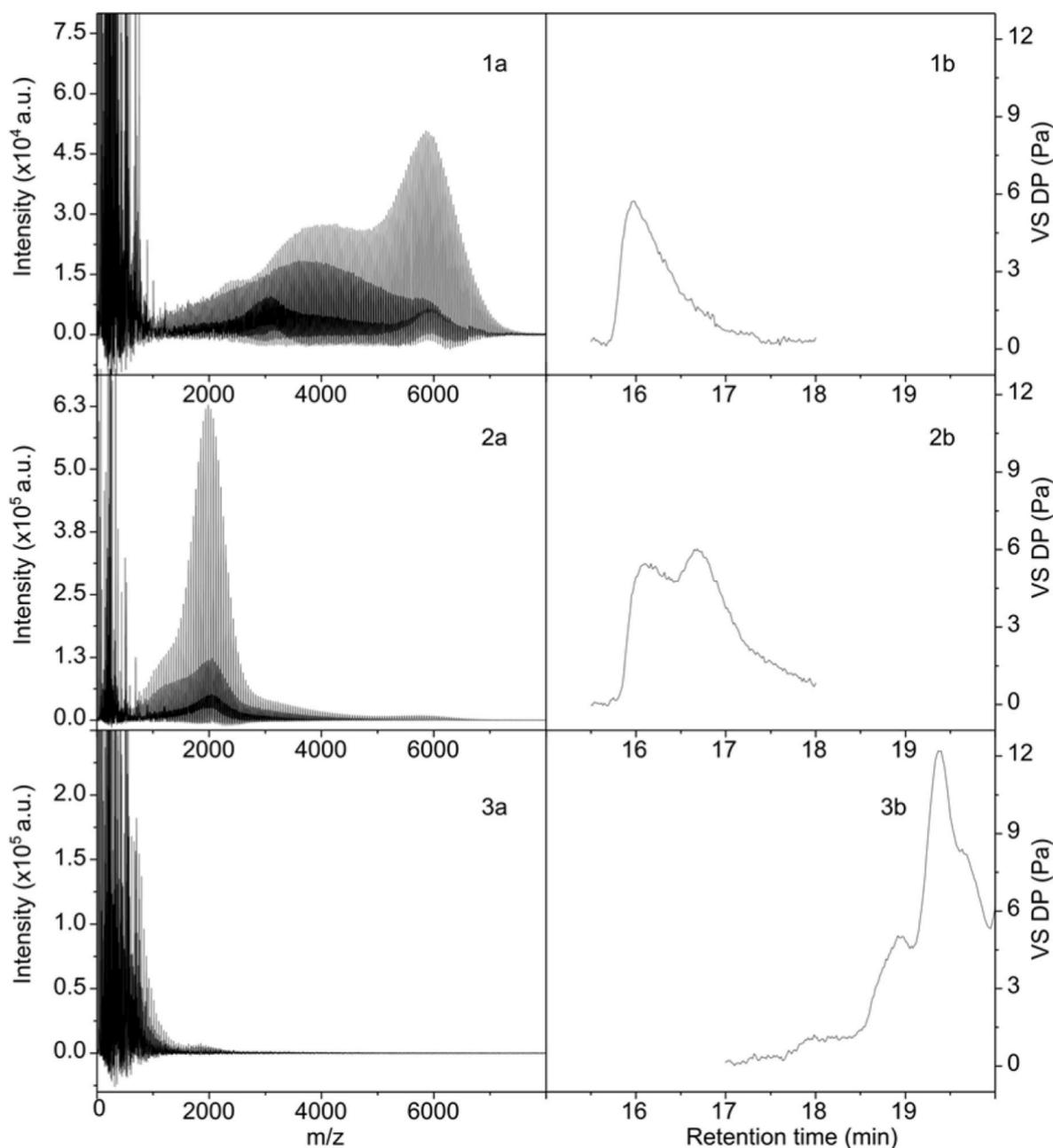


Fig. 7. A MALDI-TOF spectrum of PEG fractions extracted from wastewater influent collected from the GPC instrument 1a) Fraction 1 2a) Fraction 2 3a) Fraction 3 A GPC chromatogram of the PEG fractions extracted from wastewater influent collected at 0.1 mL min^{-1} and re-run at 1 mL min^{-1} 1b) Fraction 1 2b) Fraction 2 3b) Fraction 3.

around 500–750 Da, although accurate M_n determination was not possible due to the matrix interactions at a low molecular weight in the sample masking the PEG signal.

The overall extraction efficiency of PEG from the wastewater influent was 53%. This suggests 27% of polymer is lost due to extraction from an aqueous medium (73% extraction from distilled water), with little biodegradation and presence of low molecular weight material. The remaining 20% of PEG lost from the wastewater is therefore inherent in extracting polymer from a pseudo-environmental sample.

3.2.3. Impact of adding the extraction step

The addition of an extraction step to the GPC/MALDI-TOF method introduced new challenges in the accuracy and effectiveness of the method. The removal of polymer from an aqueous sample before its processing will create an inherent error into the method through

extraction and handling loss, as well as loss through filtration. However, if this error can be quantified, the polymer concentration can be adjusted to reflect this and the original concentration estimated. Such steps are necessary in environmental analysis, where the error associated with not only the sample medium but with the extraction of the target compound from this medium is unavoidable.

Using the method for the separation and quantification of polymer extracted from distilled water allowed the error associated with the extraction process to be explored. The extraction of 73% of the polymeric material confirms the intrinsic error associated with this additional step, which would be necessary for any aqueous environmental sample. Perhaps more unexpected was the trace amount of degraded PEG in the third fraction mass spectrum, which is attributed to biodegradation. This conclusion is supported by studies showing that PEGs are biodegradable, and highlights the additional complexity in

media where biodegradation may occur (Bernhard et al., 2008).

Following the assignment of the extraction error, the error associated with environmental material is necessary to test the applicability of the extraction/GPC/MALDI-TOF method to environmental analysis of WSPs. The comparison of the PEG standards, extracted distilled water and extracted wastewater chromatogram, highlight these additional challenges such as biodegradation, sorption and loss through filtration. The extraction of 53% of the original polymer standards signifies the 20% additional error assigned to an environmental sample as opposed to a “clean” aqueous sample.

This additional loss of polymer from the wastewater sample implies further method development is needed to improve the extraction efficiencies. With a greater efficiency, the method could be applied to non-spiked wastewater samples, for the monitoring of WSPs pre- and post-treatment. As well as the significance of the method for wastewater monitoring, its applicability to freshwater analysis has not yet been tested. This could allow the detection, characterisation and quantification of WSPs in the environment and therefore what polymers could pose a threat to freshwater organisms and consequently tested for toxicity.

4. Conclusions and outlook

GPC/MALDI-TOF is a viable method to separate and quantify PEG standards, with an accuracy of 10%. Further studies on different polymers and molecular weights, alongside a variety of matrices will provide a more general error for wider applications of the method. This error will be heavily dependent on the types of polymers investigated and how they separate within the GPC.

Quantification of polymer in a personal care product presents a greater challenge through the presence of non-polymeric material. Despite this, the method allows PEG fractions to be quantified to a high degree of confidence, based upon PCP formulation literature. This demonstrates that GPC/MALDI-TOF can be used for products that are widely used and likely to present in wastewater treatment and potentially freshwater. This method could therefore be used to monitor these products and their environmental fate.

The method can also be used to extract PEG from wastewater, where further challenges and sources of error were evident, including the presence of solids, DOM and biological activity within the sample. The lower extraction efficiency demonstrates that additional development is needed to decrease the loss of polymer in aqueous environmental samples. However, the identification of these errors is essential if environmental concentrations are to be predicted and polymers of concern to be identified.

The development of this method presents new avenues in WSP characterisation and quantification in consumer products and environmental samples. The separation and quantification of other WSPs of a greater ecotoxicological concern, as well as reduced biodegradation, is yet to be explored. The development of an aqueous GPC method would be a significant advantage in this endeavour, which is ongoing in our laboratory.

Given the lack of appropriate analytical techniques, the GPC/MALDI-TOF method provides the ability to measure and quantify WSPs. Therefore, in situations where their quantification may be important, such as in environmental monitoring, the methods as described can be used to assess the environmental prevalence of WSPs and aid their regulation.

Author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data supporting the results presented in this article are freely available via the Cardiff University Data Catalogue at <http://doi.org/10.17035/d.2023.0292450822>.

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Appendix A. Supplementary data

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