Joint Research Programme
BTO 2023.013 | December 2022

Three potential analytical methods to make invisible polyacrylamide visible in the aquatic environment

Joint Research Programme

KWR

Bridging Science to Practice

Analysis of Polyacrylamide

Three potential analytical methods to make invisible polyacrylamide visible in the aquatic environment

BTO 2023.013 | December 2022

This research is part of the Joint Research Programme of KWR, the water utilities and Vewin.

Project number
402045/244

Project manager
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Client
BTO - Thematical research - Chemical safety

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Quality Assurance
Thomas ter Laak

Sent to
This report is distributed to BTO-participants .

A year after publication it is public.

Keywords
Polyacrylamide

Year of publishing
2022

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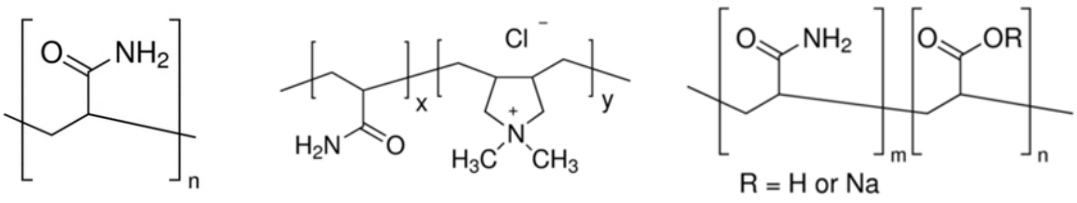
Managementsamenvatting

Drie potentiële analysemethoden om onzichtbaar polyacrylamide zichtbaar te maken in het aquatisch milieu

Auteur(s) . Ruud Steenbeek, Nienke Meekel, Erik Emke, Roan Streefland, Elvio Amato, Patrick Bauerlein .

Samenvatting: Polyacrylamide (PAM) is een overkoepelde term om alle polymeermengsels aan te duiden die acrylamidemonomeren (als een van de bestanddelen) in het polymeer bevatten. PAM kan aanwezig zijn in afvalwater van olie- en gasoperaties, in uitspoeling van landbouwgronden en in oppervlaktewateren die verontreinigd zijn door lozingen of lekkage van afvalwater. PAM's die worden gebruikt als vlokmiddel bij de behandeling van afvalwater en de productie van drinkwater, hechten zich aan deeltjes of blijven gedeeltelijk opgelost in de waterfase. Door het gebrek aan kennis over de productie, het gebruik en de specifieke toepassing zijn emissies van PAM grotendeels onbekend. Bovendien ontbreken ook de gegevens over het voorkomen van PAM-polymeren, -oligomeren en -monomeren grotendeels. Deze studie beoogt de evaluatie van enkele van de bovengenoemde analysetechnieken voor de bepaling van PAM in waterige matrices om het voorkomen in het aquatische milieu, de verwijdering (of emissie) door waterbehandelingstechnologieën, de blootstelling van het milieu en de mens en de effecten van PAM te kunnen beoordelen. Dit gebeurt door het experimenteel evalueren van uit de literatuur geselecteerde PAM-detectietechnieken in watermonsters. Het was niet mogelijk de PAM-concentraties in de watermonsters te kwantificeren, waardoor verder onderzoek nodig is naar de mogelijkheden om PAM's in drinkwater en het aquatisch milieu te bepalen.



Figuur I: De molecuulstructuur van cationisch, anionisch en non-ionische PAM

Belang: Het gebruik, blootstelling en emissies van PAM is onbekend

Door het gebrek aan kennis over de productie, het wijdverbreide gebruik en de specifieke toepassing zijn de emissies van PAM grotendeels onbekend. Bovendien ontbreken ook de gegevens over het voorkomen van PAM-polymeren, -oligomeren en -monomeren grotendeels. Deze studie beoogt de evaluatie van enkele van de bovengenoemde analysetechnieken voor de bepaling van PAM in waterige matrices

Aanpak: Drie methodes om PAM te meten zijn getest

Drie methoden om PAM op te sporen in waterige monsters worden geëvalueerd. Deze studie beoogt de evaluatie van drie analysetechnieken voor de bepaling van PAM in waterige matrices om het voorkomen in het aquatische milieu, de verwijdering (of emissie) door waterbehandelingstechnologieën, de blootstelling van het milieu en de mens en de effecten van PAM te kunnen beoordelen. Deze technieken zijn Liquid-Chromatography-Mass Spectrometry (LC-MS) gecombineerd met non-target screening, HPLC-UV en thermogravimetrische analyse. Voor de LC-MS- en HPLC-UV-analyse wordt ook een stikstofdigestiemethode gebruikt om reactiefragmenten van deze kit op te sporen

Resultaten: Het detecteren van PAM blijft lastig

Er zijn drie methoden gebruikt om PAM in water op te sporen en te kwantificeren. Ten eerste werd in dit project de stikstofdestructiemethode in combinatie met LC-MS/MS en UV-detectie gebruikt. Het was mogelijk om de reactieproducten van het gefragmenteerde PAM na gebruik van de stikstofkit kwalitatief te detecteren, maar de bepaling van de concentratie polyacrylamide-type polymeren was niet mogelijk vanwege de hoge achtergrondconcentraties van deze verbindingen wanneer geen PAM was toegevoegd. Daardoor kon ook geen correlatie worden gelegd tussen het stikstofgehalte en de PAM-concentratie. Ten tweede werd omgekeerde-fase hogedrukvloeistofchromatografie met UV-detectie toegepast. Met de HPLC-UV-methode konden enkele verbindingen worden gedetecteerd die verband zouden kunnen houden met de afbraak van PAM's door de stikstofontsluitingskit, maar het was niet mogelijk de potentiële afbraakproducten te identificeren en deze in verband te brengen met de concentraties van het polymeer van het type polyacrylamide. Ten derde werden TGA-GC/MS-analyses uitgevoerd, die inzicht gaven in de detectie van verscheidene verbindingen, waarbij het mogelijk was fragmenten van cationisch en niet-ionisch PAM te detecteren, maar niet om de concentratie of de polymeergrootte te kwantificeren.

Toepassing:

Het was niet mogelijk de PAM-concentraties in de watermonsters te kwantificeren, maar wij konden de reactieproducten van de stikstofdigestiekit na analyse in de LC-MS/MS detecteren. Verder onderzoek is nodig naar de mogelijkheden om PAM's in drinkwater en het aquatisch milieu te bepalen. Een extra stap zou het gebruik van dialyse kunnen zijn om verschillende fracties polymeergrootte van polyacrylamide te scheiden, en te concentreren op kortere polymeren die waarschijnlijk beter oplosbaar zijn in een waterige oplossing, en dus gemakkelijker te detecteren zijn. Dit zou een waardevolle nieuwe ontwikkeling zijn om inzicht te krijgen in de verspreiding en de concentraties van PAM's in het milieu en het drinkwater.

Het Rapport

Dit onderzoek is beschreven in het rapport *Three potential analytical methods to make invisible polyacrylamide visible in the aquatic environment* (BTO-2023.013)

Contents

1 Introduction

Polyacrylamide (PAM) is loosely used to describe any polymer mixtures that contain acrylamide monomers (as one of constituents) in the polymer (Paktinat et al., 2011). PAM is highly water-absorbing and is forming a gel when hydrated, for example in diapers (Bai et al., 2010). Polyacrylamides with only acrylamide monomers is non-ionic. The presence of other monomers can make the polyacrylamide either anionic or cationic. The molecular weight of the polymer ranges from 10^5 to 10^7 Dalton. The high molecular weight PAM (>10^6 Dalton) has a wide range of applications in environmental systems due to its high viscosity. PAMs are used in different sectors, but one of their main application is as a flocculant in wastewater treatment plants. They are also used as a viscosity enhancer in oil recovery and more recently as a friction reducer in high volume hydraulic fracturing and as a soil conditioning agent in agricultural applications and other land management practices (Xiong et al., 2018). PAM can be present in wastewater generated from oil and gas operations, in runoff from agricultural lands, and in surface waters contaminated by accidental spills or wastewater leakage. PAMs that are used as flocculants during wastewater treatment and drinking water production, sorb either to particulate matter or partially remain dissolved in the aqueous phase. Once they reach the ecosystems, they can follow several interrelated routes of fragmentation caused by biodegradation, oxidation, hydrolysis, photodegradation or mechanical processes. Some of these fragments can be mineralized while other persist. PAM can also partly degrade which leads to acrylamide monomer, a known toxin and potential carcinogen, in the environment (Carere, 2006). The Food and Drug Administration (FDA) and the U.S. Environmental Protection Agency (EPA) regulate acrylamide in water intended for human consumption, limiting its concentration to 0.5 µg/L, while the European Commission (EC) has a stricter limit of 0.1 µg/L. Even though PAM is classified as non-toxic to the natural ecosystems, it significantly increases water viscosity and causes movement inhibition, decreased filtering rates and disruption of food capture mechanisms for aquatic life (Hashmet et al., 2014).

Since the beginning of the 20th century, non-natural polymers and synthetic materials have progressively entered our lives, with a steady growth in variety, volumes, applications and amount of non-degradable waste (Swift et al., 2002). PAM facilitate a direct or indirect release into the environment by discharge of PAM in sewage systems. Also due to rain runoff, PAM that is released into the environment may enter sewage systems or are discharged into surface waters. These water-soluble polymers are not registered under REACH (regulation, evaluation, authorization and restriction of chemicals) and because PAM is soluble in water, it is not included in the definition of microplastics defined by the European Chemical Agency (Arp et al., 2019). While there are no treatment strategies that have been specifically developed for treating PAM/PAM residues, many of the existing water treatment processes are presumably effective for the removal and/or degradation of PAM. Information on PAM production volumes and occurrence in the environment is limited or not freely available because PAM is not registered under REACH.
Several methods have been applied to isolate and detect PAMs in aquatic samples. PAMs can for example be analyzed by reverse-phase High Performance Liquid Chromatography (HPLC), with UV detection directly from aqueous samples, with a Limit of Detection (LOD) of 5 µg/L. Additionally, PAM can be analysed by GC-MS after isolation by solid-phase extraction. However, the GC-MS method requires large sample volumes (i.e. 0.5 L). Another technique used is ion-exclusion chromatographic separation followed by MS detection (Cavelli et al., 2014). Hou et al. (2020) presented a study of the feasibility of nitrogen digestion method (Figure 1) for different kinds of polyacrylamide-type polymers such as partially hydrolysed polyacrylamides, sulfonated polyacrylamides and cationic polyacrylamides. A modified nitrogen digestion method was set up by combining the nitrogen digestion with the hydrolysis and use infrared spectroscopy (a method based on the measurement of the interaction of infrared radiation with matter by absorption, emission or reflection) to determine the polymer concentrations regardless of the hydrolysis reaction of polymers in application processes. The nitrogen digestion method is an effective way for determining the concentration of polyacrylamide-type polymers. Coupling these two method is more sensitive.

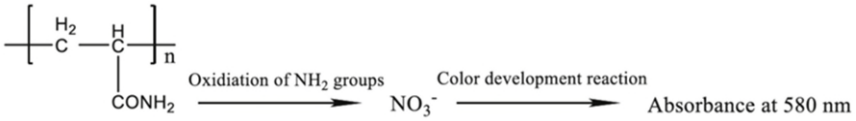


Figure 1: The mechanism of the nitrogen digestion to determine polymer concentration, including the oxidation of amide group to nitrate ions and the color development reaction (Hou et al., 2020).

Researchers have long been attempting to find new methods to determine the fate of the polymer after use. In practice the intrinsic toxicity of the polymer released to the environment is reduced by many factors, so the inability to trace these synthetic polymers and determine their spread through surface waters is a severe limiting factor. The lack of knowledge on production, the widespread use and specific application make that emissions of PAM are largely unknown. In addition occurrence data of PAM polymers, oligomers and monomers are also largely absent. This study aims at evaluating some of the analytical techniques mentioned above to determine PAM in aqueous matrices to be able to assess the occurrence in the aqueous environment, removal (or emission) by water treatment technologies, environmental and human exposure and effects of PAMs. This is done by experimentally evaluating PAM detection techniques selected from literature in aqueous samples.

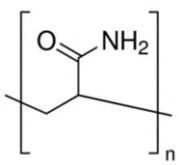
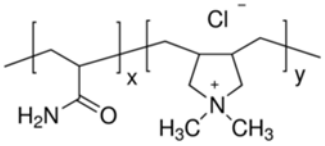
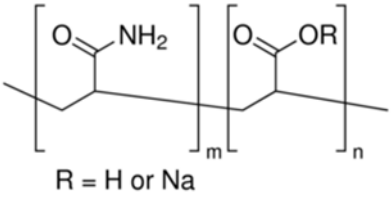
2 Materials and methods

Three analytical methods were tested. First, the nitrogen digestion method was applied to digest the PAM polymers. Subsequently, non-target screening (NTS) was applied to detect PAM polymers prior to digestion and the residues of the PAM after the nitrogen digestion to determine polyacrylamide-type polymer concentration in drinking and surface. Secondly, this nitrogen digestion method is coupled with UV-detection and finally, thermogravimetric analysis (TGA) was applied without prior digestion to detect PAMs in aqueous samples.

2.1 Materials and reagents

The reference standards bentazon-d6, atrazine-d5 and benzotriazole-d6 were purchased from Lipomed AG (Lipomed, Arlesheim, Switserland). Acetonitrile and methanol (ultra-gradient HPLC grade) were obtained from Boom B.V. (Meppel, the Netherlands). The three PAMs (see Table 1) and the Spectroquant® Nitrogen (total) Cell Test were purchased from Sigma Aldrich (Merck Life Science NV, Amsterdam, The Netherlands). The mass labeled reference standards were prepared at a concentration of 100 mg/L and further diluted to 100 µg/L in acetonitrile. All the PAMs were diluted in ultrapure water (18.2 MΩ/cm, ELGA LabWater, Lane End, UK).

Table 1: The non-ionic, cationic and anionic PAM used in this project.

Type of PAM	Name	Molucular weight	Molecular formula	Molecular structure
Non-ionic PAM	Polyacrylamide	71.08 x n	$(C_3H_5NO)_n$	
Cationic PAM	Poly(acrylamide-co-diallyldimethylammonium chloride) solution	232.753 x n	$(C_8H_{16}N{\cdot}C_3H_5NO{\cdot}Cl)_n$	
Anionic PAM	Poly(acrylamide-co-acrylic acid) partial sodium salt	237.185 x n	$(C_9H_{12}NNaO_5)_n$	

2.2 Sample preparation

Stock solutions

Stock solutions were prepared by adding 15 mg of respectively the non-ionic, cationic and anionic PAM in one liter of ultrapure water.

PAM digestion

Three stock solution were made with non-ionic, cationic and anionic PAM with a concentration of 15 mg/L. After this, the Nitrogen Cell Test was used to digest the sample and reveal detectable molecules. In brief for digestion: 10 ml of this sample was pipetted in an empty cell and 1 blue microspoon of Reagent N-1K was added. After mixing 6 drops of Reagent N-2K was added and the cell was tightly closed and mixed. The cell was heated in an preheated thermoreactor at 120 ^{o}C for one hour. After one hour, the cell was cooled down to room temperature by ambient air. The cell was shaken briefly after ten minutes. For the preparation of the measurement sample 1 mL of the digested and cooled sample was added into a reaction cell containing sulfuric acid. Also 1 mL of Reagent N-3K was added. The cell was closed again and mixed.

HRMS detection

After a reaction time of 10 minutes, 1 µg/L of the internal standard was added to the cell before analysis in the Orbitrap Fusion. First a stock solution of the nonionic, the cationic and the anionic PAM of 15 mg/L was tested to see if the reaction products could be detected in the samples. After this a dilution gradient was made and a calibration curve of 0, 3.75, 7.5 and 15 mg/L was made to try to quantify the PAM concentration in the solution.

HPLC-UV detection

For the HPLC-UV the solution after all steps of the Nitrogen Cell Test kit was used and filtered over an 0.45 µm filter. Before analysis, this solution was diluted 1000, 10000 and 10000 times respectively. Also a solution only containing reagents N-1K, only N-2K and a solution with N-1K and N-2K were analyzed. Then 20 mL of the filtered sample is let through an Oasis HLB column with a sample exchanger. The Oasis HLB column is connected to the analytical column, where the compounds in the sample are separated. By using UV-absorption the compounds are detected.

Gravimetric sample preparation

For the TGA measurements, the 15 mg/L stock solution of the three PAMs were prepared for analysis. The solutions were added to aluminum oxide cups in the following way:

Table 2: PAM samples analysed in the TGA with their volume and weight.

Sample name	V added of polymer solution [cm^3]	w polymer [µg]
211220_PAM_390_cation_1	0.390	5.85
211220_PAM_300_cation_2	0.300	4.50
211220_PAM_500_cation_3	0.500	7.50
211220_PAM_390_anion_1	0.390	5.85
211220_PAM_390_neutral_1	0.390	5.85
211216_30min_PAM_neutral_1	0.900	13.5
211216_30min_PAM_neutral_2	1.100	18
211216_30min_PAM_cation_1	0.900	13.5

All the samples were dried over the weekend covered in aluminum foil and after drying, 20 µl of polystyrene-D8 and PMMA-D8 was added to the samples (7,5 mg/L) and served as internal standard.

2.3 Method description

2.3.1 Liquid-Chromatography-Mass Spectrometry

A Tribrid Orbitrap Fusion mass spectrometer (ThermoFisher Scientific, Bremen, Germany) provided with an electrospray ionisation source was interfaced to a Vanquish HPLC system (ThermoFisher Scientific, Bremen, Germany). Every batch run mass calibration was performed using a Pierce ESI positive ion calibration solution. The ion transfer tube temperature and the vaporizer temperature were set to 300 °C. The sheath, auxiliary and sweep gas were maintained at arbitrary units of 40, 10 and 5 respectively. The source voltage were set to 3000 V in positive mode and -2500 V in negative mode. The RF lens was set to 50% and the scan range was set in the range of 50-1000 m/z. The Orbitrap resolution was set to 120,000 FWHM and the quadruple isolation was used for acquisition with a 5 ppm mass window. Data dependent acquisition was performed with a High Collision Dissociation (HCD) of 20, 35 and 50% respectively. For the chromatographic separation a XBridge BEH C18 (2.1 x 150 mm, 2.5 µm, column XPi) was used. Mobile phase A consisted of ultrapure water with 0.1% formic acid (v/v) and mobile phase B consisted of acetonitrile with 0.1% formic acid (v/v). The gradient remained at 5% B for the first minute and then increased linear to 100% in 24 minutes. The column was equilibrated at 100% B for 4 minutes and after that back to 5% B in 0.5 minute and remained at 5% for 0.5 minute. This results in a total scan time of 30 minutes. The flow rate was 0.25 mL/min and the injection volume was 100 µL. To further analyze the samples, Compound Discoverer (CD) can be used for non-target screening data processing. By finding information about the mass and chemical structures of PAM-like polymers, these polymers (or their reaction product after the nitrogen digestion kit) can be identified.

2.3.2 HPLC-UV

All the samples were analysed on a Shimadzu Prominence HPLC-UV system (Shimadzu, Kyoto, Japan) equipped with a diode-array detector and a fluorescence detector. A OmniSpher™ C18 (250 x 4.6 mm, 5 um) column (Varian, Palo Alto, CA, USA) with a guard column (Phenomenex, CA, USA) was used. Mobile phase A consists of ultrapure water with 0.05% formic acid and mobile phase B consists of acetonitrile with 0.05% formic acid. UV spectrum was from 200 to 350 nm and the inflection volume was 20 mL and flow rate was set to a maximum of 1.5 ml/min. Bentazon-d6, atrazine-d5 and benzotriazole-d6 were used as reference standards.

2.3.3 Thermogravimetric analysis

TGA measurements were performed using a TGA/DSC 3+ (Mettler Toledo, Hong Kong) and 150 µl aluminum oxide pans. The measurements were done under helium at a flow of 10.0 ml/min. For the GC/MS the gasses from the TGA were captured for 30 minutes with the Programmed Temperature Vaporization (PTV) injection system with a Tenax-liner, which is cooled to 5°C with the Peltier cooling system. The heating rate was 16 °C/min to 150 °C and after this with 12 °C/min to 330°C where it was held for 15 minutes. The compounds were transported to the GC-column in two minutes in pulsed splitless mode at a pressure of 90 kPa. The GC oven has a start temperature of 27°C and the compounds are separated and analyzed with a silica-based GC-column. The stationary phase is 5 %-phenyl-methylpolysiloxane (Agilent Technologies, HP-5ms).

3 Results

3.1 Liquid Chromatography – Mass Spectrometry

In the digested samples of non-ionic, cationic and anionic PAM 2,6-dimethylphenol (DMP) and 4-nitro-2,6-dimethylphenol were detected. 4-nitro-2,6-dimethylphenol is formed after a reaction of DMP with nitrogen (Figure 2). DMP (121.06 m/z) was found at the retention time of 9.63 minutes. Also a peak at 9.63 min (201.02 m/z) was found, which was probably DMP with a SO_4^- adduct. 4-nitro-2,6-dimethylphenol (166.05 m/z) was found at retention time of 15.11 minutes. The peak found at 14.43 minutes is the internal standard bentazone-d5. The non-ionic and anionic PAM had the same retention time and a similar intensity as the cationic PAM in this example. So a distinction between those three PAMs was not possible to make with the use of the Nitrogen Kit and the used method so far.

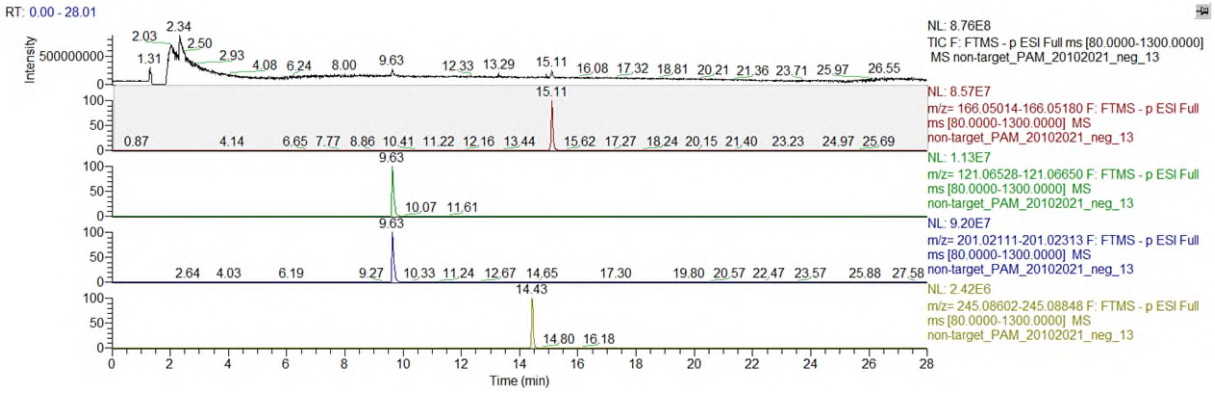


Figure 2: Results of the measurement with cationic PAM. In this example you see the detection peaks of the internal standard bentazone-d5 (RT = 14.43 min), the reaction products of the nitrogen digestion kit (DMP (RT = 15.11) and 4-nitro-2,6-dimethylphenol. (RT = 9.63 min). The other peak at RT = 9.63 min is 4-nitro-2,6-dimethylphenol with an SO_4^- adduct. The non-ionic and anionic PAM had similar results compared to the cationic PAM.

As a next step, new stock solutions were made with 0, 3.75, 7.5 and 15 mg/L of PAM to determine concentrations of these PAMs. The nitrogen digestion kit was used. With the extra nitrogen available from the PAM we tried to investigate if there was a trend visible between initial PAM concentration and the formation of 4-nitro-2,6-dimethylphenol. From these analysis with a 10 and 50 times diluted stock solution after digestion with the nitrogen kit, the intensity of DMP and 4-nitro-2,6-dimethylphenol were around $5x10^6$ when no PAM was added, and various amounts of PAM did not significantly affect the response. It seems that this was already present in the kit and was not formed as a result of breaking down of the PAM. So no trend or correlation was found between the added PAM and the formed 4-nitro-2,6-dimethylphenol (Figure 3). The method was not suitable to determine PAM concentrations by looking at the formed 4-nitro-2,6-dimethylphenol at the tested concentrations up to 15 mg/L.

From analysis by Compound Discoverer with the Non-Target Screening workflow on negative mode, 2,5-dimetylphenol was found (122.07 m/z) with the dilutions related to polyacrylamide or polyacrylamide-like polymers. After further analysis, there was no correlation found between the concentration of 2,5-dimethylphenol and the PAM concentrations of the stock solutions. This compound has also a full match with two databases. Furthermore, dodecyl sulphate was observed in the results. Dodecyl sulphate is used in cleaning procedures and for lysing cells during RNA extraction. Also 2-Hydroxymyristic acid was found, which is a protein inhibitor. These compounds were not expected and have no link with PAM or 2,4-dimethylphenol.

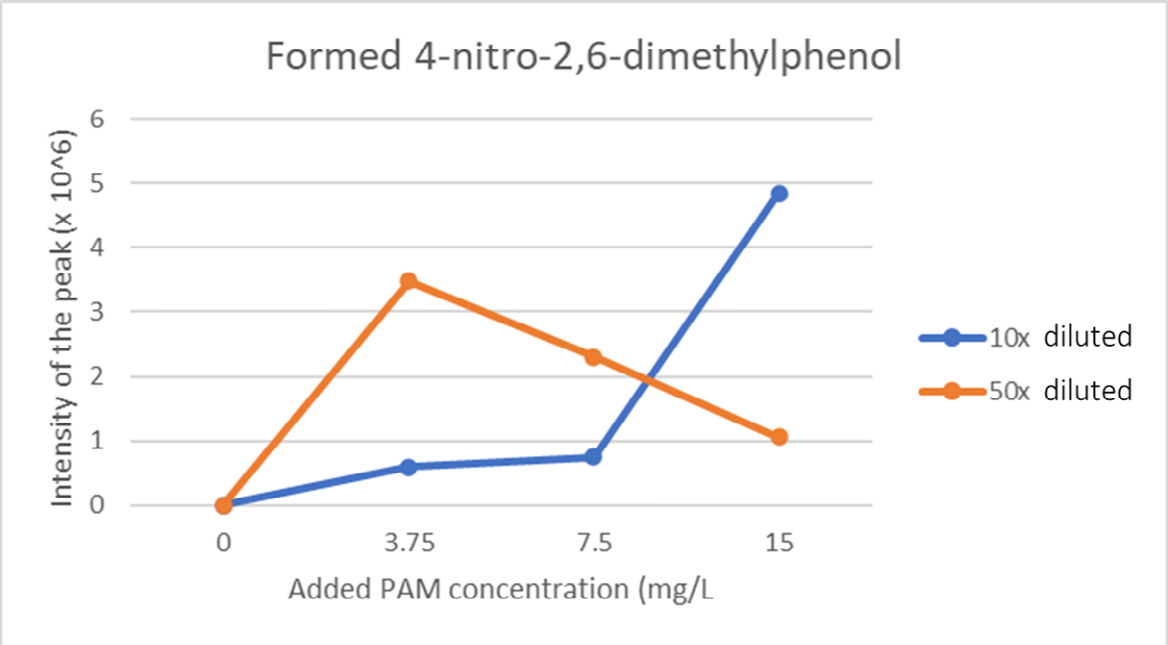


Figure 3: the peak area of the formed 4-nitro-2,6-dimethylphenol with the added PAM concentration.

3.2 HPLC-UV

Analysis of the PAM samples with PAM concentration of 0, 7.5 or 15 mg/L all showed several peaks were detected at 244 nm, which might be PAM (see Figure 4). One of the peaks shows an increase of intensity with an increased PAM concentration in the sample, which might be 4-nitro-2,6-dimethylphenol. A few peaks decreased with increasing concentration of PAM in the sample (an example is shown in Figure 5). One of these peaks might be 2,6-dimethylphenol (DMP), which reacts with nitrogen (present in PAM) to 4-nitro-2,6-dimethylphenol. But from these first measurements, we were not able to identify 4-nitro-2,6-dimethylphenol or 2,4-dimethylphenol.

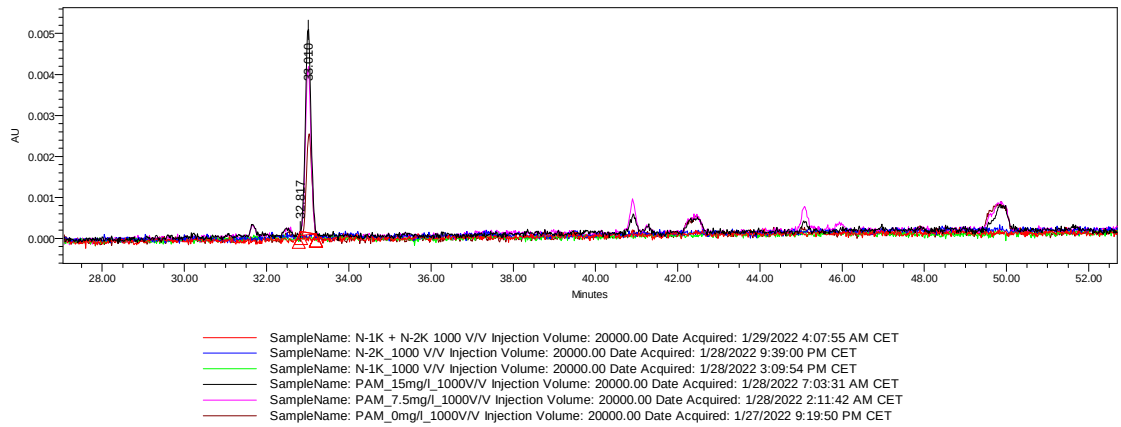


Figure 4: Spectrum analysis HPLC-UV with three PAM concentrations, reagents N-1K, reagents N-2K and the combination of N-1K and N-2K.

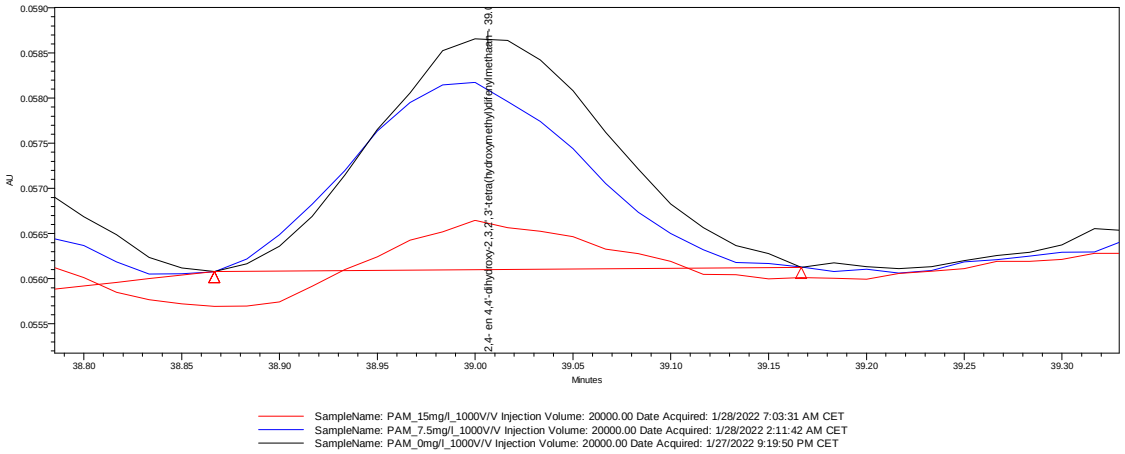


Figure 5: An example of a peak where the intensity decreased with an increasing concentration of added PAM.

3.3 Thermogravimetric analysis

3.3.1 Non-ionic PAM

After analysis of the non-ionic PAM, two possibly useful peaks were detected to identify and quantify non-ionic PAM in water samples. Glutarimide ($C_5H_7NO_2$ (NIST probability 78.7 %), retention time of 38.04 min, RI 1179), was found. The MS-spectrum of glutarimide is shown in Figure 6. When a sample with a higher non-ionic PAM was injected, a higher intensity was found (4.5E5 vs 1E5, see Figure 7).

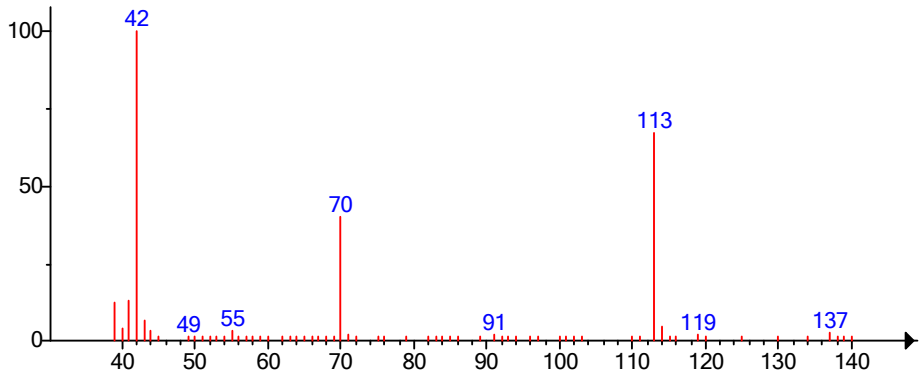


Figure 6: MS-spectrum of glutarimide

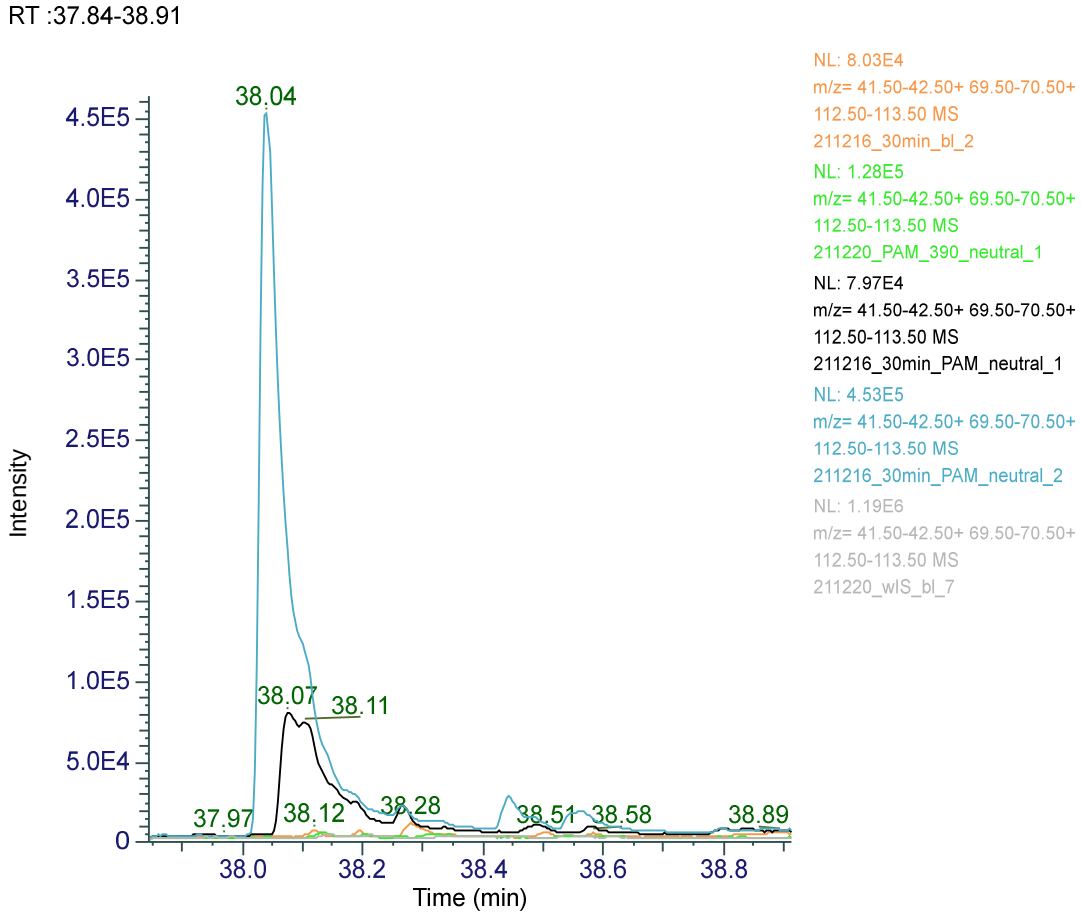


Figure 7: Extraction ion chromatogram of 113 m/z with non-ionic PAM, where a peak is visible at RT = 38.04 minutes.

At RT = 38.44 minutes (see Figure 9) another fragment is found which is related to the non-ionic PAM. Component 3,3-Dimethylpyrrolidine-2,5-dione ($C_6H_9NO_2$ (NIST probability 54.4 %). m/z 180 – 184, MS-spectrum in Figure 8). This compound is a fragment of 1,2,3-trichlorobenzene, which elutes at the same time as PAM eludes.

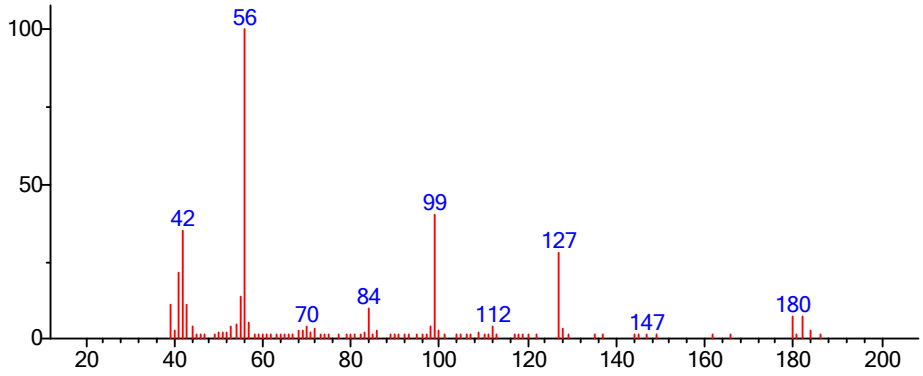


Figure 8: MS-spectrum of 3,3-Dimethylpyrrolidine-2,5-dione

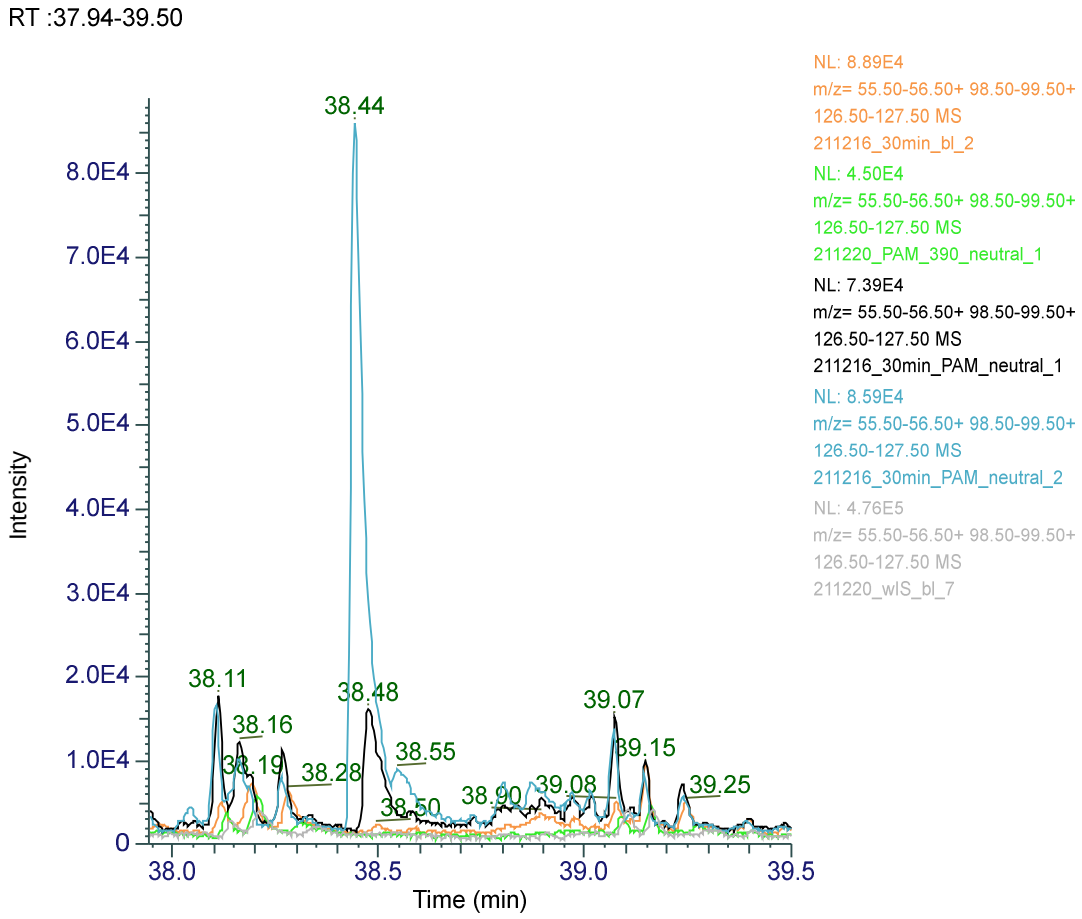


Figure 9: Extracted ion chromatogram of 56 m/z. The blue line is the 18 µg PAM and the black line is the 12 µg PAM.

Also peaks were found at RT = 35.97 minutes (Benzonitrile (NIST prob. 78%)), RT = 38.55 minutes (compound unknown) and at RT = 39.57 minutes (1,3-Diacetin (NIST prob. 65.7%)). Benzonitrile is used as a solvent and intermediate in industries making drugs, perfumes, dyes, rubber, textiles, resins, and specialty lacquers. 1,3-Diacetin is a derivative of Triacetin (T720850) which is used as a food additive and flavourings. These compounds showed an increased intensity with a higher injected concentration of non-ionic PAM (Figure 11).

3.3.2 Cationic PAM

The results of the TGA-GC/MS analysis of cationic PAM with different concentrations (see Table 2) are shown in Figure 10. The pyrolytic products from the cationic mostly seems to be ketones without any nitrogen components after pyrolysis. The components found that can be used for identification and detection of cationic PAM were p-xylene, 4-cyclopentene-1,3-dione, 2-methyl-2-Cyclopenten-1-one, 3-methyl-2-Cyclopenten-1-one, 1-(3-methylphenyl)-Ethanone and 1-(4-methylphenyl)-Ethanone. For these compounds, a higher intensity was found by a higher concentration of cationic PAM.

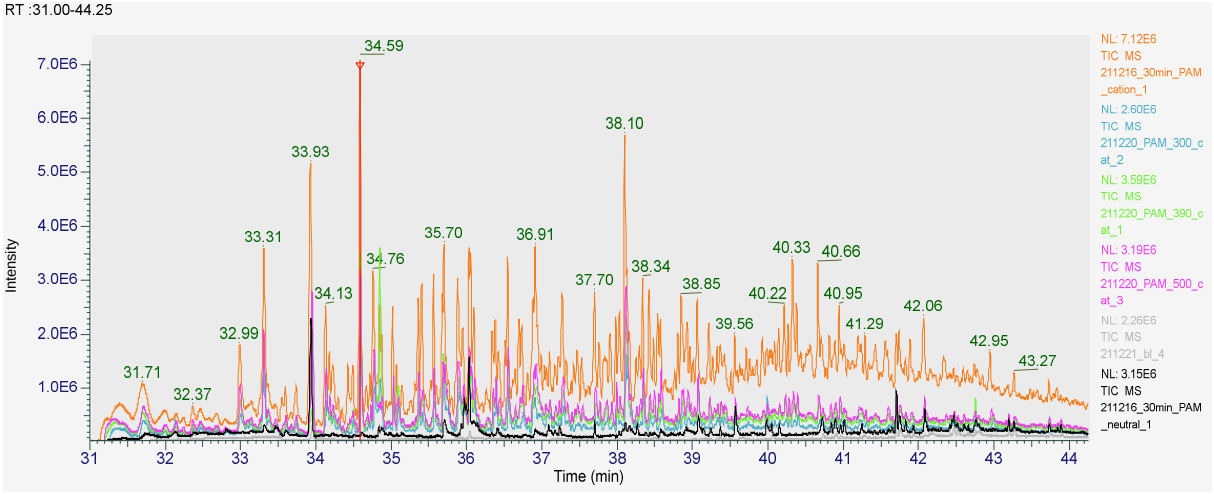


Figure 10: Extracted ion chromatogram of cationic PAM with 13.5 µg (orange), 7.50 µg (purple), 5.85 µg (green) and 4.5 µg (blue) with two instrument blanks (grey and black).

Table 3: The detected pyrolysis products of cationic PAM

Retention time [min]	Top 3 characteristic m/z values ordered by intensity		Component (NIST matching probability)	Comments
34.12	180, 107, 55		No match found	
34.59	91, 106, 105		p-xylene (39.8 %)	Matched also with other polymers like polycarbonate
34.76	96, 68, 42		4-Cyclopentene-1,3-dione (96 %)	
35.02	96, 67, 53		2-methyl-2-Cyclopenten-1-one (93 %)	
35.70	96, 67, 81		3-methyl-2-Cyclopenten-1-one (71 %)	
37.98 and 38.12	119, 91, 134		1-(3-methylphenyl)-Ethanone (28 %) en 1-(4-methylphenyl)-Ethanone (39 %) en	

3.3.3 Anionic PAM

The analysis of 5.85 µg of anionic PAM did show many peaks for detection and identification. But after analysis of the peak for retention time and mass, none of the peaks could be related to PAM or PAM derivatives. Probably, a much larger amount of anionic PAM is needed to detect and identify anionic PAM.

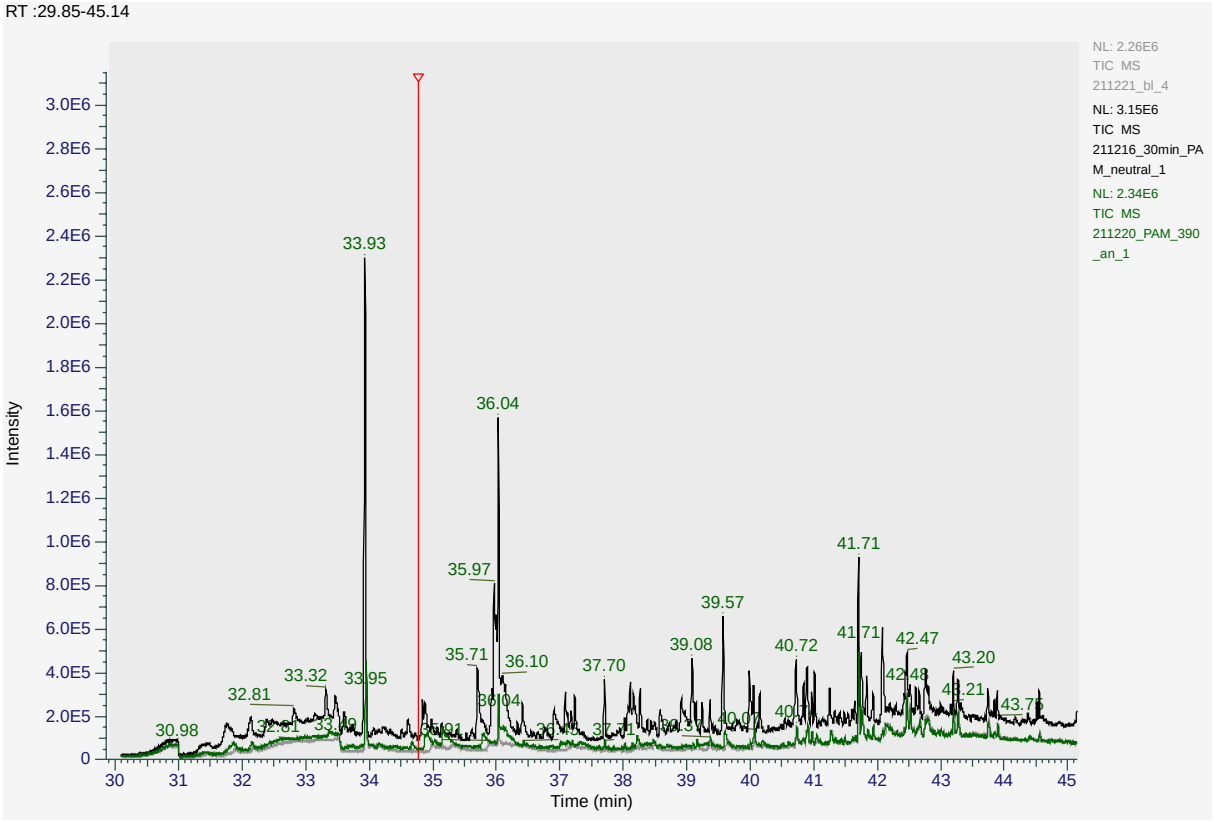


Figure 11: Extracted ion chromatogram of non-ionic PAM with 13.5 µg (black), 5.85 µg (green) and an instrument blank sample (grey).

4 Discussion

For this project, three methods were used to detect and quantify PAM in water. First, the nitrogen digestion method in combination with LC-MS/MS and UV detection was used in this project based on the study by Hou et al. (2020). It was possible to qualitatively detect the reaction products of the fragmented PAM after the use of the nitrogen kit but the determination of the concentration of polyacrylamide-type polymers was not possible due to high background concentrations of these compounds when no PAM was added. Because of this, also no correlation between nitrogen content and PAM-concentration could be made. Second, reverse-phase High Performance Liquid Chromatography with UV detection was applied based on the study by Weideborg et al. (2001). The HPLC-UV method was able to detect a few compounds which might be related to the degradation of PAMs by the nitrogen digestion kit, but it was not feasible to identify the potential degradation products and relate these to the concentrations of the polyacrylamide-type polymer. Third, TGA-GC/MS analysis were done and gave insight in the detection of several compounds, where it was possible to detect fragments of cationic and non-ionic PAM, but not to quantify concentration or polymer size. This was also found in a study where solid-phase extraction with activated carbon filter was applied to trap volatile chemicals coming from polymers upon heating. Detection was performed using Gas Chromatography and Mass Spectroscopy detection (GC-MS). This method requires large sample volumes (i.e. 0.5L) (Kawata et al, 2001).

These are a few options to analyse PAMs in aquatic environments and drinking water, but there is no standard method for detecting low concentrations of polyacrylamide in fresh water. This is due to the multiple challenges inherent in gaining the required sensitivity necessary to distinguish the hydrophilic polymer against the multitude of other dissolved and suspended environmental impurities such as humic materials and biopolymers within environmental water samples (Swift et al., 2015). Due to its high usage, concerns regarding the release of the free monomer acrylamide and concerns over the toxicity of anionic/cationic polymers to aquatic lifeforms, researchers have long been attempting to find new methods to determine the fate of the polymer after use. In practice the intrinsic toxicity of the polymer released to the environment is reduced by many factors due to degradation (e.g. exposure to light, humidity of bacteria), so whilst these polyelectrolytes are not a priority for environmental control, our inability to trace these synthetic polymers and determine their spread through surface waters is a severe limiting factor to their future use.

If PAMs are a problem in the water phase is still unclear. PAMs are strongly bound to organic matter and clay particles, and are therefore, immobile in soil and very difficult to desorb. Therefore, it is very hard to detect PAMs in the aqueous phase. This sorption process occurs rapidly and sorption affinity is very high. Subsequently, PAM is largely unavailable for biological and chemical degradation processes in the aqueous phase because PAM is a non-extractable residue (NER) (pers. Comm., 2022). NER is defined as ‘substances in soils, plants or animal which persist in the matrix after extraction in the form of the parent substance or its metabolites that are indistinguishable from naturally occurring substances’. The extraction must not substantially change the substances themselves nor the nature of the matrix (EFSA, 2015; FERA, 2012). Consequently, degradation is slow in matrices such as soil and sediment. In general, increasing molecular size and increasing chain extension lead to increased adsorption (Malik and Letey, 1991). For surface water and drinking water, it would be useful to focus on the PAMs with short chain lengths (oligomers), as those have lower affinity for geosorbents and might partially stay in aqueous solution in environmental compartments such as surface water and groundwater.

5 Conclusion and recommendations

It was not possible to quantify PAM-concentrations in the water samples, but we were able to detect the reaction products of the nitrogen digestion kit after analysis in the LC-MS/MS. Further research is needed to detect and quantify PAM-concentrations. For the TGA-GC/MS analysis, it was possible to detect pyrolytic products of the cationic and non-ionic polyacrylamide. This is a good first step in developing and validating a new analytical method to investigate PAM and other water-soluble polymers in the environment. Because there are no validated methods available yet to determine environmental concentrations of water-soluble polymers, the current situation might be comparable to early stages of microplastics research (Hubbertsberg et al., 2020). Further research is needed to investigate the possibilities to determine PAMs in drinking water and the aquatic environment. An extra step could be the use of dialysis to separate different polymer size fractions of polyacrylamide, and focus on shorter polymers that are probably more soluble in aqueous solution, and therefore more easy to detect. This would be a valuable new development to get insight in the distribution and concentrations of PAMs in the environment and drinking water to determine their occurrence and fate.

Acknowledgements

A special thanks to Joop Harmsen for providing useful literature about polyacrylamide and the conversation we had about the use, the fate and the occurrence of PAM in the aquatic environment.

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