Pontifícia Universidade Católica
do Rio de Janeiro

Brenda Duarte Gralha

Influence of polymer degradation on the analysis of polyacrylamide by total organic carbon

Dissertação de Mestrado

Dissertation presented to the Programa de Pós-Graduação em Química of PUC-Rio in partial fulfillment of the requirements for the degree of Mestre em Química.

Advisor: Prof. D.Sc. Aurora Pérez Gramatges
Co-advisor: D.Sc. Eduardo José Creatto

Rio de Janeiro
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ABSTRACT

Gralha, Brenda Duarte; Pérez Gramatges, Aurora (Advisor); Creatto, Eduardo José (Co-advisor). Influence of polymer degradation on the analysis of polyacrylamide by total organic carbon. Rio de Janeiro, 2023. 65p. Dissertação de Mestrado – Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro.

Polyacrylamide copolymers play an important role in enhanced oil recovery (EOR), whose widespread use aims to improve oil production. Assessment of polymer in the produced water is thus required for monitoring the oilfield operation and for environmental concerns. However, this task is challenging due to the matrix complexity and the possible degradation of the macromolecule during the process. Among the different methods for polymer determination, total organic carbon (TOC) is advantageous in comparison to others reported in the literature because of its low cost, easy operation and short analysis time. Due to this, a TOC method was developed for the determination of polyacrylamide content, and the influence of salinity, molar mass, and two types of chemical degradation (by hydrolysis and Fe^{2+}/O_2) on the polymer quantification through this method were explored in this work. Rheological measurements, NMR and ATR-FTIR analyses were also carried out to evaluate the extent of degradation. The polymer quantification was not affected in the presence of different salt contents. Similarly, analyses of samples with different molar masses did not affect TOC results. The hydrolysis degree of the polymers was confirmed by ^{13}C NMR and ATR-FTIR, while rheological measurements confirmed degradation by Fe^{2+}/O_2. Noticeably, both degradation mechanisms investigated did not impair polyacrylamide determination. For all factors evaluated, the errors were never greater than 8%. The results obtained highlight the TOC as a suitable and reliable method for the determination of polyacrylamide with good accuracy, showing its potential application in the analysis of real samples.

Keywords

Polyacrylamide, Total Organic Carbon, Polymer Degradation, Produced Water

RESUMO

Gralha, Brenda Duarte; Pérez Gramatges, Aurora (Orientadora); Creatto, Eduardo José (Coorientador). Influência da degradação polimérica na análise de poliacrilamida por carbono orgânico total. Rio de Janeiro, 2023. 65p. Dissertação de Mestrado – Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro.

Os copolímeros de poliacrilamida desempenham um papel importante na recuperação avançada de petróleo, cuja utilização visa o aumento da produção de óleo. A avaliação do polímero na água produzida é, portanto, necessária para monitorar a operação do campo petrolífero e para questões ambientais. Entretanto, tal avaliação é desafiadora devido à complexidade da matriz e à possível degradação da macromolécula durante o processo. Entre os diferentes métodos para determinação de polímero, o carbono orgânico total (TOC, do inglês *total organic carbon*) é vantajoso em comparação com outros métodos reportados na literatura devido ao seu baixo custo, fácil operação e curto tempo de análise. Devido a isso, um método de análise por TOC foi desenvolvido para a determinação do teor de poliacrilamida, e a influência da salinidade, massa molar e dois tipos de degradação química (hidrólise e por Fe^{2+}/O_2) na quantificação do polímero por este método foram exploradas neste trabalho. Medidas reológicas, análises de ressonância magnética nuclear (RMN) e de espectroscopia de infravermelho (ATR-FTIR, do inglês *Fourier-transform infrared with attenuated total reflectance*) também foram realizadas com o intuito de avaliar a degradação. A quantificação do polímero na presença de diferentes teores de sal não foi afetada. De modo similar, as diferentes massas molares dos polímeros não afetaram os resultados das análises por TOC. O grau de hidrólise dos polímeros foi confirmado por ^{13}C RMN e ATR-FTIR, enquanto medidas reológicas confirmaram a degradação por Fe^{2+}/O_2. Notavelmente, ambos os mecanismos de degradação investigados não impactaram a determinação de poliacrilamida. Para todos os fatores avaliados, os erros não ultrapassaram 8%. Assim, os resultados obtidos destacam o método TOC como adequado e confiável para a determinação de poliacrilamida com boa exatidão, conferindo-lhe um potencial de aplicação para análises de amostras reais.

Palavras-chave

Poliacrilamida, Carbono Orgânico Total, Degradação de Polímero, Água Produzida

SUMMARY

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LIST OF ABBREVIATIONS AND ACRONYMS

ATR-FTIR	Fourier-Transform Infrared with Attenuated Total Reflectance
DAD	Diode Array Detector
EOR	Enhanced Oil Recovery
IC	Inorganic Carbon
HPAM	Hydrolyzed polyacrylamide
HPAM-AMPS	Poly[acrylamide-*co*-(sodium acrylate)-*co*-(sodium acrylamide-2-methylpropane sulfonate)]
HD	Hydrolysis Degree
HPLC	High Performance Liquid Chromatography
NDIR	Non-Dispersive Infrared
NMR	Nuclear Magnetic Resonance
NPOC	Non-Purgeable Organic Carbon
PAM	Polyacrylamide
PAM-AMPS	Poly[acrylamide-*co*-(sodium acrylamide-2-methylpropane sulfonate)]
POC	Purgeable Organic Carbon
Rg	Radius of gyration
RMN	*Ressonância Magnética Nuclear*
SEC-UV	Size Exclusion Chromatography with UV detection
SD	Sulfonation Degree
SLS	Static Light Scattering
TC	Total Carbon
TOC	Total Organic Carbon

1 INTRODUCTION

The exploration of petroleum is an essential activity in constant growth since the use of this natural resource is very broad and comprehends many different applications. With increasing demand over the years, alternative methods arose to raise the production in mature fields. Initially, only water and/or gas was injected with the aim to sweep oil from the reservoirs, namely secondary recovery [1,2]. From the moment when too much water is produced along with very low amounts of oil, this procedure starts to become inefficient [2]. Nevertheless, due to the advances in research in this field, tertiary recovery methods took place to improve the process and overcome this, thus recovering the residual oil [1,2].

The so-called enhanced oil recovery (EOR) is inserted in this context as a tertiary method in which the use of polymers is particularly important due to its widespread and constant improvement [1–4]. Among the large variety of macromolecules existent and applicable to this purpose, polyacrylamide copolymers are one of the synthetic polymers most used by oil and gas companies [1–5].

Along with the injection of polymer, consequently, raises the need for monitoring the species throughout the stages of oil production to assess the efficacy of the EOR method [6]. Additionally, it is important to evaluate the possibility of reusing the back-produced water and to provide a proper disposal of the effluent, considering its environmental impact [5]. However, quantifying the back-produced polymer is a challenge, since it can undergo chemical and structural changes due to degradation in the reservoir and during the lifting stage, and also the presence of potential interfering factors such as surfactants, and different types of additives (e.g., corrosion inhibitors, de-emulsifiers, biocides etc.) [4,6].

As the interaction of such compounds with the polymer leads to different degradation mechanisms [5–9], their implications in the quantification methods are so far a concern [6]. For instance, hydrolysis [2,5,6,10] and chemical degradation due to the polymer reaction with iron (II) and oxygen [2,5,7–10] play an important role in this context. Nevertheless, despite the studies already reported in the literature, there is still a gap regarding the full understanding of Fe^{2+} autoxidation and polymer chain scission, especially for water matrices and sulfonated polyacrylamides. Additionally, it may be attributed to both the complex reaction mechanisms and conditions involving the generation of free radicals, and the macromolecule characteristics. Mechanical degradation, due to the action of pumps, for example, can also cause chain scission [2,5,10]. All these aspects result in a matrix (*i.e.*, the produced water) with high complexity, thus hampering the development of an accurate and quantitative method for polymer determination that is free of interferences.

Considering the abovementioned issues, the purposes of this work were to develop a quantitative method based on carbon measurements for the determination of polyacrylamide, and evaluate the influence of salinity, molar mass, and two types of chemical degradation (by hydrolysis and Fe^{2+}/O_2) on it. In face of other techniques and methods already reported in the literature [4,6], total organic carbon (TOC) was chosen to be implemented mainly due to its low cost, easy operation and low time-consuming analysis. The possibility of not being impaired by polymer chemical degradation and changes in their molar mass was also taken into account.

In light of the scope of this research, the secondary objectives comprise the following aspects:

1. Develop a reliable quantitative method (precise and accurate) that is selective for the type of polymer under study, and that allows fast analyses.
2. Assess the impact of molar mass and hydrolysis degree of the polymer on its quantification by TOC.
3. Conceive a method of polymer degradation from the reaction with Fe^{2+} in a O_2 environment and analyze the effects on the quantification of polyacrylamide using the TOC method.

This work was divided in different sections with the purpose of presenting and discussing the main topics related to the theme under study. Therefore, some theoretical aspects regarding the definitions and use of polymers in EOR will be introduced in the next section, followed by the explanation of the two main techniques employed (TOC and SEC-UV). After that, the bibliographic research is presented, comprising the use of TOC for the quantification of polymers and the main characteristics related to polyacrylamide hydrolysis and degradation by ferrous ions. The description of the materials and methods can be found in section 4, while the results and discussion will be subdivided in different parts in the fifth section, intending to provide a clear approach of each aspect analyzed and its meaning in this context.

2 THEORETICAL ASPECTS

2.1. Polymers

Polymers consist in molecules with long chains [11,12], resulting in high molar mass. For this reason, they are also referred to as macromolecules. Another characteristic of polymers is their formation by repeating units [12,13], which can have equal or different chemical compositions and properties, and its structure, which can be linear, branched or even reticulated, confer distinct characteristics to the compounds [12]. If only one type of monomer constitutes the polymer structure, it is defined as homopolymer, otherwise, as copolymer. Furthermore, they can be originated from natural sources or obtained by synthetic routes. In this work the focus will be on synthetic macromolecules, more specifically polyacrylamide (Figure 1). Synthetic polymers can be produced by several polymerization mechanisms, whose intrinsic characteristics of each process can result in polymeric chains with variable lengths. For this reason, these types of polymers are polydisperse, hence, its molar mass is usually calculated from an average value of its mass distribution [11,12].

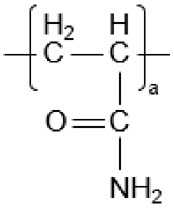


Figure 1. Polyacrylamide (PAM) chemical structure.

Regarding copolymers, there are some ways that each repeating unit can be organized and distributed along the chain structure, namely: alternating, block and random [11]. In the former, different monomers are merged one by one; in the second one, they are arranged in groups of each chemical unit and connected as blocks, and in the latter, they are randomly connected. Besides that, Canevarolo [12] also reports another type of copolymer so-called graft, which consists in the union of segments of an homopolymer to another, as ramifications. Figure 2 illustrates such generic copolymer structures. In all cases, the interaction of the species is formed by covalent bonds among the atoms [12], and the formation of these types of polymers is related to its polymerization mechanisms [11].

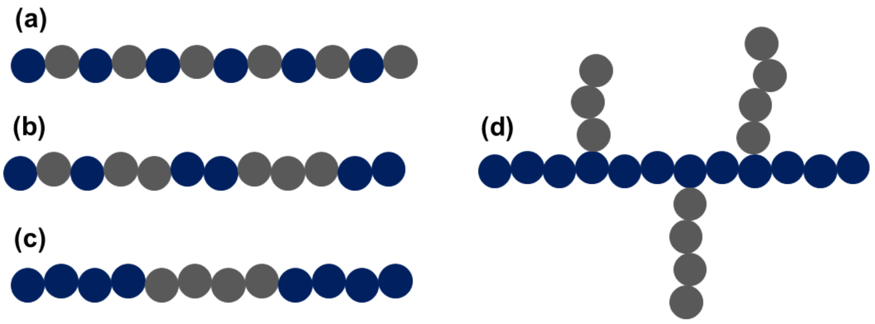


Figure 2. Representative structures of different copolymers: **(a)** alternating, **(b)** random, **(c)** block and **(d)** graft. The blue and gray circles represent different monomers of the chemical structures of the copolymers.

Possibly the most striking property of polymers is their ability to increase the viscosity of a solvent. In solution, the polymer chains tend to assume a coil conformation due to entropic reasons [12], whose size varies depending on the quality of the solvent and the temperature, *i.e.*, the interactions between polymer-polymer, polymer-solvent, and solvent-solvent molecules [11]. As the size of the polymer coil is much larger than that of solvent molecules, they hinder the flow in larger quantities, increasing the viscosity of the solutions [12]. The entanglement of polymeric chains is another factor that contributes to the increase in viscosity. The concentration at which the chains begin to become entangled is called overlap concentration, c^* [14]. Therefore, both polymer concentration and molar mass will be directly correlated to the viscosity of the samples [11]. Considering this, it is also worth mentioning that the presence of charges on the polymer structure can also influence its conformation in solution, leading to chain stretching occasioned by the electrostatic repulsion [11]. Thus, it is clear that the viscosity of a polymer solution depends on a wide range of factors: the structure of the polymer and solvent, the molar mass and concentration of the polymer, temperature, salinity, etc.

The size of a polymer chain can be determined through the radius of gyration (*Rg*) [11,15], which can be measured by static light scattering (SLS) of polymer solutions, for example [15]. This parameter represents a correlation of the average distance from the center of mass of the polymer coil to a part of its structure [11]. Additionally, it is also possible to evaluate the interaction of the solvent with the macromolecule and to determine its molar mass by SLS analysis using the Zimm model [12,15].

2.2. Application of polymers in EOR

The processes of oil production in mature fields can comprise secondary recovery or EOR methods [1,3,16]. In the former, the injection of water and/or gas inside the reservoir can be used to shift the oil that remained trapped in the porous media [1,16]. However, depending on the characteristics of the oil and the reservoir, a phenomenon so called as viscous fingering (Figure 3) may be prone to occur, being caused by a significant difference between the low viscosity of the injected fluid compared to the high viscosity of the oil. Hence, a considerable amount of oil still may not be accessed and produced when using this method [1,3].

Considering the remarkable ability of polymers to increase the viscosity of solutions even in small amounts, these molecules have been employed for various uses in the oil industry, with emphasis on EOR. In these processes, the presence of a macromolecule in the aqueous matrix contributes to the reduction of viscous fingering phenomena, resulting in a more uniform displacement (Figure 3) as the water mobility decreases in relation to that of the oil. Hence it favors the increase of oil recovery from the reservoir [1,3,16].

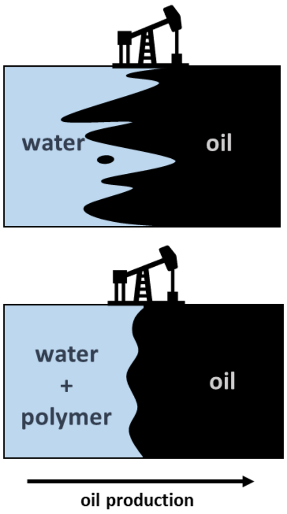


Figure 3. Representation of the reduction of the viscous fingering phenomena after the injection of polymer along with water in the reservoir, instead of just water.

Acrylamide copolymers are one of the synthetic polymers most used in EOR, especially hydrolyzed polyacrylamide (HPAM, Figure 4) [2,3,6,16]. The main reasons for its application are related to its low cost and high resistance to mechanical degradation [3], however, some factors intrinsic to the reservoir conditions can affect its physicochemical properties in solution, including temperature, salinity [2,3,16] and pH [6]. Furthermore, the hydrolysis degree (HD) of HPAM is also relevant on these procedures since changes in the viscosity of the fluid can be observed [2,6] as the polymer molar mass varies [2], thus reflecting on the efficiency of the process. Other concerns related not only to HPAM refer to the undesirable degradation mechanisms of polymers during EOR processes, which besides the abovementioned factors, may also be caused by shearing, the presence of dissolved oxygen and metal ions. Another type of polymer commonly used is poly[acrylamide-*co*-(sodium acrylamide-2-methylpropane sulfonate)] (PAM-AMPS) [2,16,17], whose sulfonated portion is reported to increase the macromolecule resistance to degradation [16,17].

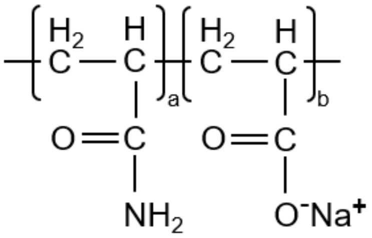


Figure 4. Hydrolyzed polyacrylamide (HPAM) chemical structure.

2.3. Total Organic Carbon

The total organic carbon technique comprehends the determination of carbon-containing species after its conversion by oxidation into a unique form, *i.e.*, carbon dioxide [18–20]. The application fields of the method may include analysis of different types of waters, soils [18,19], and polymers [6]. In general, the carbon compounds can be briefly classified as total carbon (TC), inorganic carbon (IC), total organic carbon (TOC), purgeable organic carbon (POC) and non-purgeable organic carbon (NPOC). Some authors describe each of these classes as: TC, all molecules comprising both organic and inorganic carbon sources; IC, carbonate, bicarbonate, and dissolved carbon dioxide; TOC, organic carbon compounds, either volatile or not; POC, volatile organic carbon molecules; NPOC, non-volatile carbon species left after IC and POC removal [18–20].

There are different oxidation methods [18,19] and types of carbon detection described in the literature as being designed for TOC analysis [18–20], but in this section the focus will be on the Shimadzu combustion catalytic oxidation method of carbon measurement, since the analyses done in the present work were performed in a Shimadzu TOC-L_{CPN} equipment. After evaluating the characteristics of the analytes and matrices intended to be analyzed in this work, the NPOC method was chosen and tested for the analysis of polyacrylamides.

Figure 5 summarizes the steps in the NPOC procedure. The NPOC analysis starts with the injection of a liquid sample in the equipment (step 1) to be acidified in advance (step 2), intending to ensure that all the IC content that might be present in the medium is converted to a volatile form for further elimination. Therefore, a small amount of HCl is automatically added and then the sample is sparged with synthetic air, providing IC removal in the form of CO_2. Additionally, POC contents can be either volatilized during this process. Some concerns regarding these two steps of the procedure are related to the amount of acid added, pH and sparge time. According to Bisutti, Hilke and Raessler [18], the presence of carbonates in the samples may require specific conditions in the method to be completely eliminated. For example, it was reported that the acidification of liquid samples with hydrochloric acid for 5 min would be effective to convert all the IC content to carbon dioxide, and along with a step of bubbling air in the medium, it could take 2 min. Additionally, according to Shimadzu [20] the pH value may be in the range of 2 and 3 after acidification. However, controlling this parameter may be a difficult task depending on the way of how it was performed, and the equipment used.

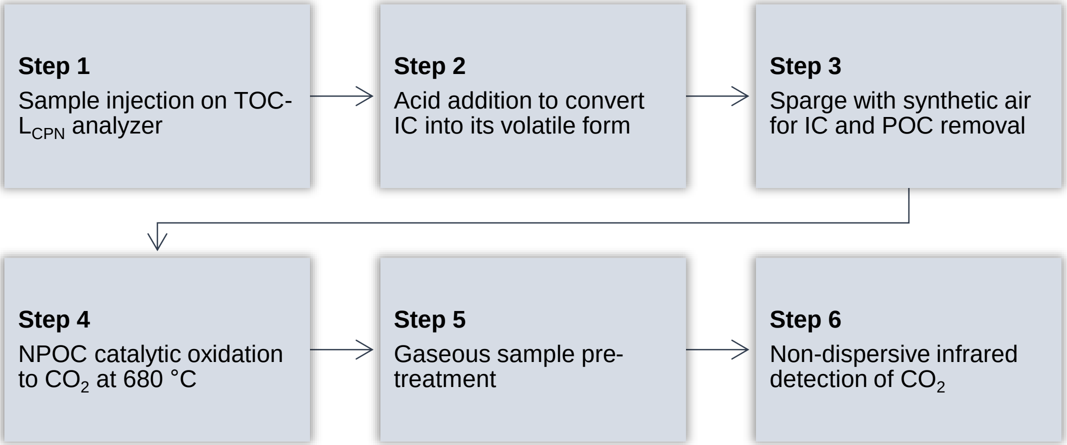


Figure 5. Steps of the carbon analysis on TOC through the NPOC method.

After the removal of IC and POC content, the carbon sources remaining in the liquid sample are therefore related only to the non-volatile carbon (*i.e.*, NPOC), which in this work corresponds to the polymer content. The sample is subsequently inserted in the combustion tube filled with a catalyst, enabling the carbon oxidation to CO_2 at a fixed temperature of 680 °C (step 4). The gaseous samples are then pre-treated (step 5), comprising the processes of cooling, dehumidification (which is attributed to be performed for eliminating water vapor before carbon detection [19]), and lastly filtration through an halogen scrubber for the removal of halogens

[20]. Finally, the CO_2 content is analyzed by infrared spectroscopy. The TOC instrument is equipped with a gas detector, namely non-dispersive infrared (NDIR), which allows measurements in the middle IR region [19], besides providing low detection limits and having a high sensibility [18,20]. As shown in Figure 6, at each analysis a corresponding peak is obtained, which can be directly integrated in the software and related to the concentration of carbon in the sample.

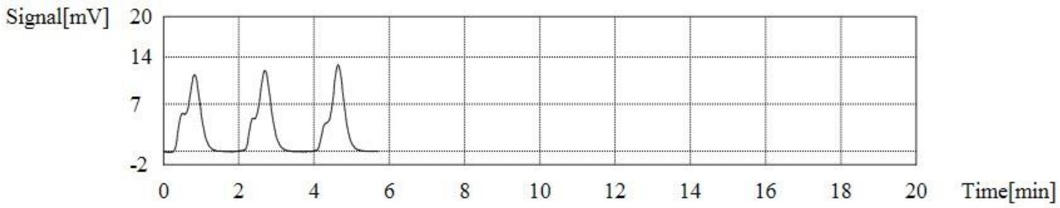


Figure 6. Illustration of a result obtained from the NPOC measurements of a 20-ppm polymer sample.

2.4. Size Exclusion Chromatography

Size exclusion chromatography is an analytical technique of separation of compounds by their molar mass [21], commonly used in the analysis of polymer samples [4,6]. The measurements are performed with a liquid chromatographer whose separation column is filled with a stationary phase composed by a porous material with variable pore sizes. Due to this, depending on the molar mass of each compound, it can be retained for a long time inside the column, or it can be more easily eluted (*i.e.*, in a shorter time) along with the mobile phase in constant flow [21]. In that sense, larger molecules are detected first, followed by the smallest ones. Therefore, distinct peaks can be observed at different retention times, which is strongly related to the hydrodynamic volume of the species. For such reasons, analyses by size exclusion chromatography are commonly used to determine the molar masses of different compounds [4].

To ensure that all the compounds intended to be analyzed will be efficiently distinguished, it is essential to set the adequate conditions and parameters for the method that fit in the purpose of analysis. The measurement of the species can be attained through different types of detection including, for example, the use of refractive index (RI) and ultraviolet (UV) detectors [6,21], while its quantification can be obtained from the correlation with a calibration curve [21]. However, when analyzing polymer samples such as polyacrylamide, the hydrolysis degree of the macromolecule has to be considered since it may change the response of the method [6].

3 BIBLIOGRAPHIC REVIEW

3.1. Total Organic Carbon analysis of polymers

The total organic carbon technique was chosen to be implemented as an alternative form to determine the polymer content of samples, especially acrylamide copolymers. As reported by Taylor and Nasr-El-Din [6], there are various techniques potentially applicable to such purpose. For example, size exclusion chromatography with UV detection (SEC-UV) [4], nitrogen digestion [22], N-bromination of amide groups [23–26] and turbidimetry [27–29] have already been used for the quantitative analysis of PAM, HPAM and/or PAM-AMPS. However, there are also different constraints related to each one, regarding varied aspects as summed up in Table 1, which can make the analysis of polymers difficult.

Considering the principles of the TOC methods and the characteristics of the samples, different kinds of analyses can be performed, as mentioned in section 2.3. Therefore, the first motivation of this work consists in the development of a TOC method that allows the quantitative analysis of polyacrylamide samples, whilst the second one is related to the possibility of this method not being affected by the main sources of interferences when analyzing real samples of produced water from oilfields, such as chemical degradation by hydrolysis and Fe^{2+}/O_2 reaction, and changes in the polymer molar mass.

Table 1. Comparison of some of the alternative methods for polymer quantification reported in the literature.

Article	Polymer	Method of polymer quantification	Disadvantages
Espinosa *et al.* [4]	PAM-AMPS	SEC-UV	• Affected by the hydrodynamic volume of the polymer • Hydrolysis of the polymers can provide changes in the molar mass of the polymer, consequently affecting its hydrodynamic volume • Presence of compounds in the matrix with same hydrodynamic volume of the analyte that could absorb in the same wavelength of the polymer
Hou, Han and Fuseni [22]	HPAM	Nitrogen digestion	• Presence of nitrogen compounds in the matrix that could absorb in the same wavelength of the analyte
Taylor [23]; Taylor *et al*. [24,25]; Lu and Wu [26]	PAM, HPAM	N-bromination of amide groups	• Bromine and cadmium iodide toxicity • Presence of amine and/or amide groups other than the polymers' • Hydrolysis of the polymers can result in the loss of amide groups • The presence of species in the matrix that could absorb in the same wavelength of the analyte • Presence of some surfactants from EOR processes
Kuehne and Shaw [27]; Allison, Wimberly and Ely [28]; Kang *et al.* [29]	PAM, HPAM	Turbidimetry	• HD of the polymers can affect the sensitivity of the method • Presence of anionic surfactants and high contents of organic carbon may interfere, generating overestimated results

Some studies reported in the literature were selected to be discussed in this section concerning the applications of TOC for the determination of polymers. One of the works evaluated was reported by Kokufuta *et al.* [30], in which the polymer content in the samples was determined after performing tests of polymer adsorption onto silica gel. Although the authors did not use acrylamide copolymers, TOC measurements were carried out to analyze the macromolecules under study. The method chosen consisted in the subtraction of IC from TC and two carbon standards (potassium biphthalate and sodium bicarbonate) were used for the construction of the calibration curves for further quantification of polymer. Additionally, prior to the carbon analyses the samples were acidified with one drop of HCl 6 N to avoid interferences that would occur from incorporation of atmospheric CO_2 in the medium. Based on the data obtained, the authors disregarded the possibility of interference of the IC content on TOC and claimed that the method was adequate for the intended purposes. However, the correlation of the TOC content with the results from the elemental analysis of the macromolecule and how the polymer concentration was obtained remained unclear.

Hou, Han and Fuseni [22] reported a comparative analysis between TOC and a nitrogen digestion method implemented for the determination of polyacrylamide. Differently from the previous study discussed, in this work the authors constructed a calibration curve ranging from 20 to 500 ppm of HPAM with 40% HD. Considering the context presented, it may be presumed that the samples analyzed were prepared in brine. However, no information regarding this supposition or the possible influence of the salt content on the TOC equipment was presented. Furthermore, there was a lack of information regarding some of the conditions used in the TOC method. The authors reported the agreement of TOC and nitrogen digestion analyses related to the polymer concentration as a function of the volume injected into the core, as the values obtained for the dynamic adsorption of the polymer were similar (0.051 and 0.053 mg/g-rock, respectively). Nevertheless, this study highlights the use of TOC for the analysis of polyacrylamide samples, although it is notable the need for more information regarding the conditions applied and possible constraints.

Xiong *et al.* [31] reported carrying out NPOC analysis of synthetic flowback water. The matrix contained polyacrylamide (10 MDa), used as a friction reducer polymer in hydraulic fracturing processes. It was not clear, however, how the calibration curve was constructed, *i.e.*, if polymer samples or standard carbon solutions were used. The samples were previously diluted in water to fit in the calibration curve; however, the concentration range was not provided. Although not mentioned in the experimental procedure, the authors also analyzed synthetic samples of fracturing fluids by TOC. From the comparison of the results obtained it was observed a reduction of the TOC content from fracturing fluid to flowback water samples. The interpretation of such data was not completely understood, nonetheless the phenomena observed seems to be attributed to the adsorption of the polymer on shale. As can be seen, once again not much information of the method was given, and in this case, it may be because the TOC analyses were not the main objective of the study.

Conduction of the bibliographic research regarding the use of TOC methods for the analysis of polymers showed that there is a lack of studies presenting in a proper way the rationale behind the method development, as well as its benefits and drawbacks. Most of the literature on this topic focuses on analyzing various types of water and soil samples [18,19], being out of the scope of this work, and because of this, only a few studies were discussed.

As can be seen, the application of TOC methods for determining polymer contents in aqueous samples is still not well established and consolidated in the literature. In most of the cases there are not many explanations regarding the limitations and/or benefits of the method. Additionally, the parameters and conditions of the method used are not always completely specified, which hinders the reproduction of similar studies or even complementary ones intending to propose advances in this research area. Therefore, it emphasizes the gap existent in the literature over this field, highlighting the relevance of the present work developed due to its contribution for the scientific community.

For this reason, this work is focused on the development of a TOC method that can effectively quantify polyacrylamide copolymers in aqueous samples, with the aim of enabling its application in the analysis of real oilfield samples.

3.2. Chemical degradation of acrylamide copolymers

Aligned with the objectives of this work, this section provides a brief literature review on the two types of polymer degradation to be further studied: hydrolysis and chemical degradation by Fe^{2+}/O_2. The main purpose is to gain a better understanding of how these mechanisms occur, intending to assess its effects on the determination of polyacrylamide samples by TOC analysis.

Hydrolysis is a very common form of degradation of acrylamide polymers, being prone to occur at different pH [5,31], and temperatures [5,17,31]. In the case of macromolecules such as PAM-AMPS, some authors reported that along with the formation of carboxylic acids from hydrolysis of the acrylamide repetition unit, the amide group linked to the sulfonate portion (AMPS) could also undergo hydrolysis [5,17], being converted to ammonia-2-methylpropanesulfonic acid [5], as shown in Figure 7.

Considering this, changes on the polymer molar mass and on the viscosity of samples should be expected, which could interfere with the polymer quantification even though no chain scission occurs in such degradation mechanism. In fact, the circumstance of not having chain scission in the polymer structures after hydrolysis is advantageous for the TOC analysis, indicating that no interferences on the quantification of the macromolecule would occur. Hence, it is inserted in the context of this work as another motivation for implementing the TOC method on the analysis of HPAM-AMPS with the aim to evaluate the effect of hydrolysis on the polymer quantification.

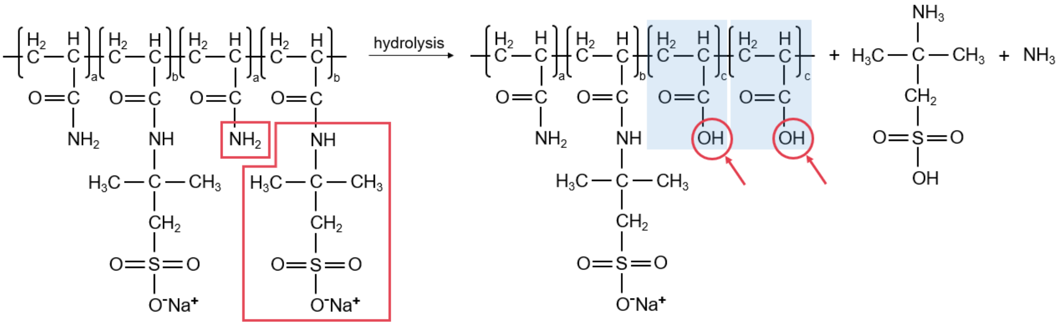


Figure 7. PAM-AMPS degradation by hydrolysis.

Based on the analysis of HPAM by nitrogen digestion, Hou, Han and Fuseni [22] proved, for example, that the macromolecules with higher HD presented a larger decrease on their nitrogen content related to the amide groups. Additionally, the authors also demonstrated that it is possible to determine by infrared spectroscopy the HD of different polyacrylamides, including HPAM and PAM-AMPS. For both types of polymers, with increasing HD value, the intensity of the peaks from acrylamide and acrylic acid varied. While the intensity of the $CONH_2$ peak decreased with higher HD, that of COOH presented a slight increase on its intensity, thus allowing to stablish a correlation of these signals to the extent of hydrolysis using a calibration curve to determine the HD values.

According to Vieira *et al.* [17], the analyses of PAM-AMPS in different brines and thermal conditions showed that for temperatures in the range of 70 to 100 °C, the polymer can undergo hydrolysis, resulting in HD values varying from 25 up to almost 70%. However, these results are strongly correlated to the composition of the brine. For example, although it was observed that the polymers could present thermal stability in some cases, under harsh conditions (*i.e.*, solutions containing high content of divalent salts in the brine composition and submitted to high temperature (100 °C)), it was observed the precipitation of the polymer and a lower HD value of 20% was determined. Additionally, the authors also performed some aging tests to evaluate the chemical degradation. From the analyses of acrylamide copolymer samples (Flopaam AN 125) in two types of brines, Vieira *et al.* [17] observed that, at 100 °C and after almost one year, the 25% content of AMPS reduced in the order of 15% and 60% for brines 1 and 2, respectively (in this case, brine 2 presented a higher content of salts). Furthermore, besides these analyses the authors also showed the suitability of carrying out ^{13}C NMR measurements to characterize the polymers, and elemental analysis to determine its HD, as performed for different polyacrylamides.

As could be observed, the procedures discussed [17,22] highlight the importance of knowing the HD of the macromolecules, since it can provide changes on the polymer samples. Therefore, depending on the method used to quantify the polymer, the hydrolysis degree of the macromolecules should always be determined when the HD values are not known, or even to confirm the reference values if standard hydrolyzed polymers are used. Hence, it could avoid obtaining overestimated values of polymer concentration. Considering these aspects, in this work the hydrolysis degree of PAM-AMPS is going to be analyzed prior to the TOC measurements by both infrared spectroscopy and ^{13}C NMR analyses.

Differently from hydrolysis, degradation by Fe^{2+}/O_2 is not expected to occur inside the reservoir due to the addition of oxygen scavengers, which prevent the oxidative reaction. However, the relevance of the degradation mediated by iron for the present study lies in the analysis process of produced water. When water is sampled and brought into the laboratory, it inevitably comes into contact with atmospheric oxygen, which can react with any Fe^{2+} present in the matrix and facilitate the degradation of the macromolecule.

Fe^{2+}/O_2 degradation involves a complex set of steps, resulting in significant structural changes, such as a reduction in molar mass. Free radicals such as hydroxyl and peroxyl are generated in the solution due to the autoxidation of ferrous ion, which strongly depends on the pH and the content of Fe^{2+}, as shown in the following mechanisms of reaction (Equations 1-6) [8,31].

$Fe^{2+} + O_2 \rightarrow Fe^{3+} + \cdot O_2^-$ **Equation 1**

$\cdot O_2^- + H^+ \rightarrow \cdot OOH$ **Equation 2**

$Fe^{2+} + \cdot OOH \rightarrow Fe^{3+} + HO_2^-$ **Equation 3**

$HO_2^- + H^+ \rightarrow H_2O_2$ **Equation 4**

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH$ **Equation 5**

$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^-$ **Equation 6**

Once the free radicals are formed, they can react with the polymer in solution, initiating the formation of polymer radicals and the chemical degradation of the macromolecule. Gröllmann and Schnabel [32] reported that polyacrylamide could be degraded at three different regions by hydroxyl radicals present in the medium (not generated by Fe^{2+}/O_2), possibly leading to the formation of formaldehyde. The probable sites for reaction were pointed by the authors as being related to the carbons α and β to the carbonyl group, and the nitrogen atom from the amide group. Considering this, from the latter it should not be expected to occur polymer chain scission, as the carbon-carbon bounds would not be affected.

Considering the aim of this research, the abovementioned study can be correlated to the chemical degradation of polymers by the autoxidation of ferrous ions in the presence of dissolved O_2, as reported by Xiong *et al.* [31]. In light of this, the authors proposed a scheme for this mechanism of polyacrylamide degradation, suggesting a possible pathway for this reaction considering the attack by free radical on the carbon β to the carbonyl group (Figure 8). It is worth mentioning that in this study, the authors intended to analyze the degradation of polyacrylamide in the presence of shale in samples from hydraulic fracturing processes. The presence of Fe^{2+} is intrinsic to the matrix due to dissolution of shale, which corroborates to the formation of free radicals in the medium that could degrade the polymer at high temperatures.

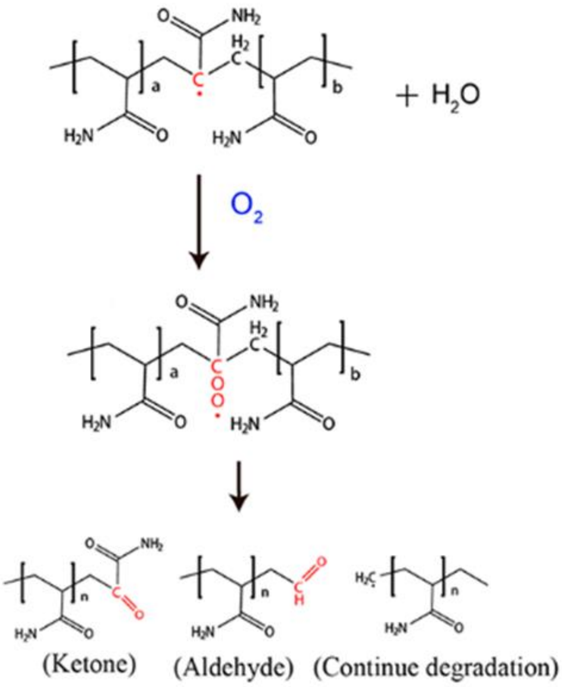


Figure 8. Possible mechanism of PAM chemical degradation by the autoxidation of Fe^{2+} in the presence of dissolved O_2 (**source:** reprinted (adapted) with permission from Xiong *et al.* [31]. Copyright 2018 American Chemical Society).

After analyzing the samples by infrared spectroscopy, Xiong *et al.* [31] identified some by-products from the reaction performed at 80 °C, suggesting the presence of aldehyde, ketone, and carboxylate groups. In that sense, it could indicate that part of the polymer chain was broken into smaller fragments as a result of the macromolecule degradation. Additionally, the occurrence of acid hydrolysis was also reported by the authors, whose effect increased at pH 4 and 80 °C. Also regarding this, the results obtained by infrared spectroscopy suggested that the carboxylate groups formed were not linked to any other species such as sodium.

As sulfonated polyacrylamides were analyzed in the present work, it is noteworthy that due to their chemical structure, more probable reactive sites should be expected to be available for the attack of free radicals, consequently leading to the polymer degradation. Hence, the effects from this could be expected to be more pronounced, *i.e.*, the PAM-AMPS chains could be broken in more parts in contrast to PAM, once there are considerable contents of Fe^{2+} and dissolved oxygen available for the reaction. Most importantly, as this type of degradation depends on the pH, as previously mentioned, considering the possible reactive sites formed in the polymer structure reported by Gröllmann and Schnabel [32], the hydrolysis of the macromolecule could also occur along with the chemical degradation by Fe^{2+}/O_2, as suggested by Xiong *et al.* [31].

Ramsden and McKay [8] studied the degradation of polyacrylamide caused by the autoxidation of Fe^{2+}, whose work was considered as a reference for this study. An extensive investigation of the mechanisms correlated with the polymer degradation was presented by the authors, but only part of the research is going to be discussed next intending to correlate the tests carried out with the purpose of the present study. The authors investigated the degradation of PAM in the presence of 20 ppm of ferrous ions under initial conditions of O_2 saturation. Different pH conditions were also adopted to measure the extent of degradation by viscosity measurements of the polymer samples after 2, 4 and 6 days of reaction at 20 °C and ambient O_2. Regarding the results, it was observed that the duration of the reaction led to an expressive loss in the viscosity of the PAM aqueous samples, and that the pH of the samples had a remarkable influence on it. At pH values between 6 and 7, the reduction in the viscosity of the samples reached almost 40% in the 6th day, while in the 2nd day it was near to 20%. Therefore, the determination of the polymer concentration in samples submitted to such mechanisms of chemical degradation should be restricted to the use of methods that are free of such potential interfering factors, aiming to obtain accurate and reliable results.

Other studies carried out for polymer samples in brine also proved the macromolecule degradation by the same mechanism. For example, Ferreira and Moreno [10] measured the viscosity of hydrolyzed polyacrylamide samples that were stored at stainless steel bottles. After 14 days, the degradation reached 53% in the presence of 17.2 ppm of iron, whilst after 45 days and for 26 ppm of iron, the extent of degradation was 74.2%. In contrast, when storing the sample in a beaker in the presence of 4.4 ppm of iron, no degradation was observed. The authors also observed that the color of the degraded solutions changed to yellow and orange, respectively, which is another indicative of the oxidation of Fe^{2+}.

Considering all the aspects presented, it is noticeable that both mechanisms of chemical degradation can have a remarkable influence on the polymer structure, hence representing a potential interfering factor on its determination by different analytical methods. Therefore, it highlights the importance of investigating its effects on the method chosen to analyze the polymer samples, which in this study concerns TOC. In this context, it is worth mentioning the difficulty on finding studies in the literature comprising the application of TOC analysis for the quantification of polymers also considering the effects of hydrolysis and degradation by Fe^{2+}/O_2.

4 MATERIALS AND METHODS

4.1. Materials

All polymers used in this work are listed in Table 2, and their chemical structure are represented in Figure 9. The main polymer studied (PAM-AMPS 1) was obtained from Equinor through a partnership research project, while the others were kindly donated by SNF. The reagents required for the analyses and the TOC and HPLC equipment conditioning were purchased from Sigma-Aldrich: hydrochloric acid (37%), ferrous chloride tetrahydrate (≥99%), sodium chloride (≥99%), calcium chloride dihydrate (≥99%), magnesium chloride hexahydrate (≥99%), potassium chloride (≥99%), and sodium phosphate monobasic dihydrate (98-100.5%, HPLC grade). Synthetic air from Linde Gases Brasil and Messer Gases Brasil was also used in the TOC analyzer as carrier and purge gas.

Table 2. List of polymers employed in this work.

Polymer	**Code**	**Molar Mass / MDa**	**Sulfonation Degree (SD) / mol%**	**Hydrolysis Degree (HD) / %**	**Supplier**
FLOPAAM AN 125	PAM-AMPS 1	8.0	25	-	SNF
FLOPAAM AN 125 VLM	PAM-AMPS VLM	1.5-3.0	25	-	SNF
FLOPAAM AN 125 MPM	PAM-AMPS MPM	3.0-5.0	25	-	SNF
FLOPAAM AN 125	PAM-AMPS 2	5.0-7.0	25	-	SNF
FLOPAAM AN 125 SH	PAM-AMPS SH	7.0-10.0	25	-	SNF
AN 125 AA 5 LM	HPAM-AMPS LM5	10.0	25	5	SNF
AN 125 AA 5 VLM	HPAM-AMPS VLM5	5.8	25	5	SNF
AN 125 AA 10 LM	HPAM-AMPS LM10	8.5	25	10	SNF
AN 125 AA 10 VLM	HPAM-AMPS VLM10	5.0	25	10	SNF

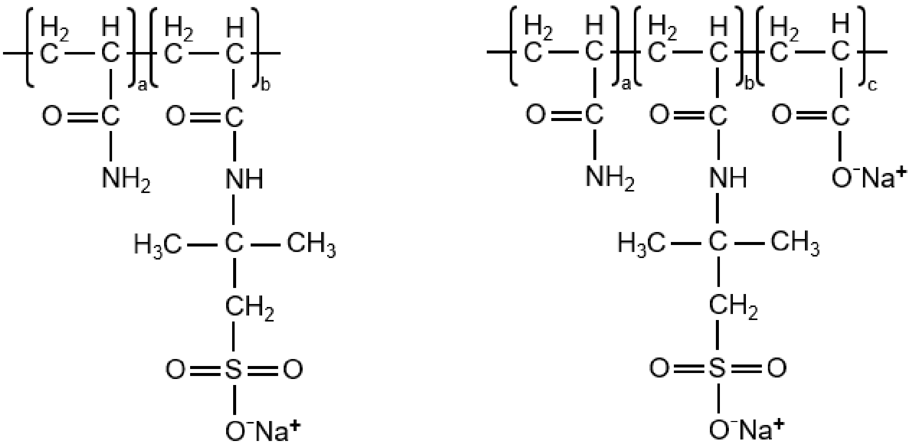


Figure 9. Chemical structure of PAM-AMPS (left) and HPAM-AMPS (right) type of polymers. The indexes a, b and c refer to the molar quantity of each repetition unit in the polymer composition.

4.2. Sample preparation

The solid reagents used for sample preparation were weighed on analytical balances (Mettler-Toledo MS204TS/A00 and XPE603S/A) and dissolved in ultrapure water from a Milli-Q® Direct 8 filtration system (18.2 MΩcm at 25 °C, TOC = 2 ppb), except for the polymer samples prepared in brine.

- **Synthetic produced water (brine)**

The synthetic produced water was prepared by weighing salts individually to obtain the concentrations specified in Table 3, using composition and concentrations typically found in produced water of heavy oil fields [4]. This gives a salt content in the brine of around 10 wt.%.

Table 3. Composition of the synthetic produced water.

Salt	Concentration / $g{\cdot}L^{-1}$
NaCl	86.6
$CaCl_22H_2O$	10.0
$MgCl_26H_2O$	6.3
KCl	0.6

(**Source:** adapted from Espinosa *et al.* [4])

- **Mobile phase for HPLC**

One liter of mobile phase was prepared for HPLC measurements by dissolving 5.999 g of NaH_2PO_4 with deionized water in a volumetric flask. The solution was filtered on a proper filtration system for mobile phase using a Millex-FH [LME1] membrane (0.22 µm) and then was stored in a bottle glass.

- **Polymer solutions**

Polymer solutions were obtained by weighting the solvent and then adding the desired polymer. For instance, to prepare 1 L of a stock solution with concentration of 1,000 ppm of PAM-AMPS 1, 1,000 g of ultrapure water was weighed in a 2 L beaker on a balance. With the water under constant stirring on a magnetic plate, about 1 g of the polymer was gradually added into the vortex formed in the beaker. This procedure is strictly essential to avoid the formation of gel lumps while the powder is being dissolved in water, and to ensure that the final concentration of the solution is correct. At the end of this process the stock solution was kept under magnetic stirring overnight to assure the complete homogenization, and then it was stored in an amber glass bottle. The PAM-AMPS 1 stock solution in brine was prepared in the same way but using the synthetic produced water as solvent.

In order to construct a calibration curve with the TOC analyzer, an aliquot of the 1,000 ppm PAM-AMPS 1 stock solution (in water) was diluted to 100 mL and 40 ppm of polymer. This sample was injected in the equipment and automatically diluted to obtain the 6-point calibration curve ranging from 1 to 20 ppm.

For the chromatographic analysis, each diluted polymer solution was prepared individually in 50 mL volumetric flasks, corresponding to one point of the calibration curve. This curve was constructed with five concentration levels in the range of 5 and 25 ppm of PAM-AMPS 1 in water.

The nine samples used for checking the linearity of the TOC were diluted in volumetric flasks (50 mL) from 1 to 80 ppm, considering that the TOC equipment only supports automatic dilutions in the magnitude of fifty times. For the study of the salinity as a potential interfering factor on the polymer quantification method by carbon measurement, 10-ppm polymer samples with 1 and 10 wt.% of salt were prepared. For the former, a 100-ppm stock polymer solution in brine was diluted to 50 mL with the synthetic produced water, aiming to preserve the salt content; for the latter, the same stock solution was diluted with ultrapure water.

For the ^{13}C NMR analysis, about 0.8-1.0 mL of D_2O brine (86,6 g·L^{-1} of NaCl) was used to dissolve 30 mg of the polymers (HPAM-AMPS LM5, HPAM-AMPS VLM5, HPAM-AMPS LM10 and HPAM-AMPS VLM10). Prior to the measurements, the samples were transferred to 5 mm NMR tubes.

4.3. Polymer chemical degradation by Fe^{2+}/O_2

The study of the polymer chemical degradation in water through its reaction with Fe^{2+} ions in the presence of dissolved oxygen was developed considering the method described by Ramsden and McKay [8]. In one of the experiments, the authors evaluated the polyacrylamide (PAM) degradation at 0.5% (5,000 ppm), O_2 saturated conditions and varying the pH of the samples, after reaction with ferrous ammonium sulfate and oxygen at 20 °C. The PAM used had a HD <0.3% and a molar mass of 5.6×10^6 Da [7,8]. Based on this procedure, some adaptations were employed in this work as described in the following.

First, a 1,000 ppm PAM-AMPS 1 stock solution in water was used to carry out this test. Once this mechanism depends on the availability of oxygen in the sample, the solution was kept under constant bubbling of compressed air during 24 h to afford O_2 saturation before the addition of ferrous ion. After that, a 20,000-ppm solution of Fe^{2+} was prepared by dissolving the proper amount of $FeCl_2 \cdot 4H_2O$ to 25 mL with ultrapure water. An aliquot of 0.1 mL of this stock solution was added to a 100 mL volumetric flask, which was then filled with the polymer solution, O_2 saturated the day before.

Intending to assess the extent of the chemical degradation in a short period of time, the final sample was kept under O_2 saturation for 3 days and this procedure was carried out in duplicate. After 48 and 72 h, aliquots of the sample were collected for TOC analyses and rheological measurements. Prior to carbon measurements, the samples were filtered (0.22 µm hydrophilic Millex syringe filter) and diluted to 10 ppm with ultrapure water (final volume equals 50 mL). Additionally, the pH of samples was qualitatively measured using pH-indicator strips.

4.4. Total Organic Carbon

The polymer determination by TOC measurements was conducted through the non-purgeable organic carbon (NPOC) method on a Shimadzu TOC-L_{CPN} instrument coupled with one OCT-L 8-Port Sampler. The equipment also has a regular sensitivity catalyst and a non-dispersive infrared (NDIR) detector for gases. Shimadzu TOC-Control L software (version 1.06) was used for data acquisition, and the equipment settings used in the analysis are shown in Table 4**.**

Table 4. TOC-L_{CPN} settings used in the analyses of polymer samples.

Parameter	Value
Carrier gas flow / mLmin^{-1}	150.0
Sparge gas flow / mLmin^{-1}	80.0
Gas pressure / kPa	200.0 ± 10
Furnace temperature / °C	680

The construction of the calibration curve and the analyses were conducted by the NPOC method, as previously described in Section 2.3. In the development of this method, some parameters were set as default, namely maximum standard deviation (0.1000), maximum coefficient of variation (2.00%), and peak acquisition time. The other conditions were predefined: injection volume of 100 µL, at least 3 up to 6 measurements per sample for multiple injections, acid addition rate of 3%, sparge time of 1.5 min and double washing of the injection lines with the respective sample to be analyzed.

When intending to analyze polymer samples on TOC analyzer using an OCT-L 8-Port Sampler, the viscosity of the solutions may hamper the injection in the instrument. As the capillaries are extremely thin, it may require that samples with high viscosity are diluted.

A 6-point calibration curve was constructed (in triplicate) for the PAM-AMPS 1 quantification, once the areas obtained by carbon measurements on TOC analyzer are correspondent to the polymer content in the samples. The curve was designed in the range of 1-20 ppm, which enables quantification of sufficiently low polymer concentration and also higher ones (>20 ppm) through dilution of concentrated samples.

4.5. Size Exclusion Chromatography with UV detection

To compare the quantification of polymer by TOC, another method, based on high performance liquid chromatography (HPLC), was also employed. For this purpose, the tests were carried out on an Agilent 1260 Infinity II chromatographer with a PSS SUPREMA Ultrahigh column (300 x 8 mm; particle size of 10 µm). The method of size exclusion chromatography with UV detection (SEC-UV) was applied according to the optimized conditions proposed by Espinosa *et al.* [4] and summed up in Table 5, but using a diode array detector (DAD). All diluted samples were filtered using a Millex hydrophilic syringe filter (0.45 µm) and then transferred to the 2 mL vials prior to the injection. Agilent OpenLab software (version 2.5) was used for the acquisition of chromatograms and additional data.

Table 5. HPLC settings used in the analyses of polymer samples.

Parameter	Value (description)
Column temperature / °C	30
Mobile phase / mol·L^{-1}	0.05 (NaH_2PO_4)
Wavelength / nm	205
Injection flow rate / mL·min^{-1}	1.0
Injection volume / µL	50
Data acquisition time / min	40

All the chromatographic analyses of polymer samples were carried out by Daniel da Silva Vicente (LASURF – PUC-Rio). The quantification of the polymer content of the samples was performed by integrating the respective peak to obtain the corresponding value of area. Finally, the concentration of polymer was determined using a calibration curve and the peak area of the analyte.

4.6. Rheology

For the evaluation of polymer chain scission due to the reaction with ferrous ion at a O_2 saturated environment, rheological measurements were performed on a Thermo Scientific HAAKE Mars 60 rheometer, coupled with a water bath allowing tests under different temperature conditions. Once degradation occurred, it would imply on changes in the solution viscosity. Thus, after 48 and 72 h of aging, rheological analysis of the samples was carried out using a double-gap geometry (CC27 DG/Ti) and a 4 mm gap. Additionally, a polymer sample saturated with O_2 but without Fe^{2+} addition was also analyzed for further comparison.

The flow-curves were obtained at a shear rate ranging from 0.018 to 1,000 s^{-1} at a fixed temperature of 25 °C, and before the tests each sample was placed in the equipment to reach temperature equilibrium for 300 s. Thermo Scientific HAAKE RheoWin Job Manager and Data Manager software were used for setting parameters and data acquisition, respectively.

4.7. Nuclear Magnetic Resonance Spectroscopy

Intending to confirm both HD and SD, the sulfonated polyacrylamide samples were analyzed by 13-carbon nuclear magnetic resonance (^{13}C NMR). The measurements were carried out on a Bruker Ascend^{TM} 400 spectrometer, using a pulse sequence of zg90, a relaxation delay of 15 s and 7,200 scans. Additionally, the decoupler mode was inverted to avoid the nuclear Overhauser effect. According to the chemical shift signals obtained in the carbonyl regions correspondent to amide, AMPS and carboxylate groups, the area of their integrals (A_{CONH_2}, A_{CONHSO_3} and A_{COO^-}, respectively) was used to calculate the HD and SD through Equation 1 and Equation 2.

$$HD\ (\%) = 100 \cdot \frac{A_{COO^-}}{A_{COO^-}+A_{CONH_2}+A_{CONHSO_3}}$$ **Equation 1**

$$SD\ (\%) = 100 \cdot \frac{A_{CONHSO_3}}{A_{COO^-}+A_{CONH_2}+A_{CONHSO_3}}$$ **Equation 2**

These experiments were carried out in partnership with the laboratory Central Analítica Pe. Leopoldo Hainberger (CAPLH) from PUC-Rio by Álvaro J.P.. Sample preparation and data processing was done with help of M.Sc. Cecília Cavalcanti (LASURF – PUC-Rio).

4.8. Fourier-Transform Infrared Spectroscopy

For some polymers, the hydrolysis degree was determined by Fourier-transform infrared spectroscopy with attenuated total reflectance (ATR-FTIR), based on the method reported by Hou, Han and Fuseni [22]. The solid compounds were analyzed without any pre-treatment and the measurements were performed in a Bruker ALPHA II FT-IR spectrometer.

The main parameters of the method were set as: resolution of 2 cm^{-1}, 128 scans and wavelength range from 400 to 4,000 cm^{-1}. The software Bruker OPUS Viewer was used for data acquisition. The analyses and data processing were carried out with help of Diogo Gomes (CAPLH – PUC-Rio) and M.Sc. Cecília Gonçalves (LASURF – PUC-Rio).

5 RESULTS AND DISCUSSION

5.1. Determination of PAM-AMPS by TOC: method development and pre-validation

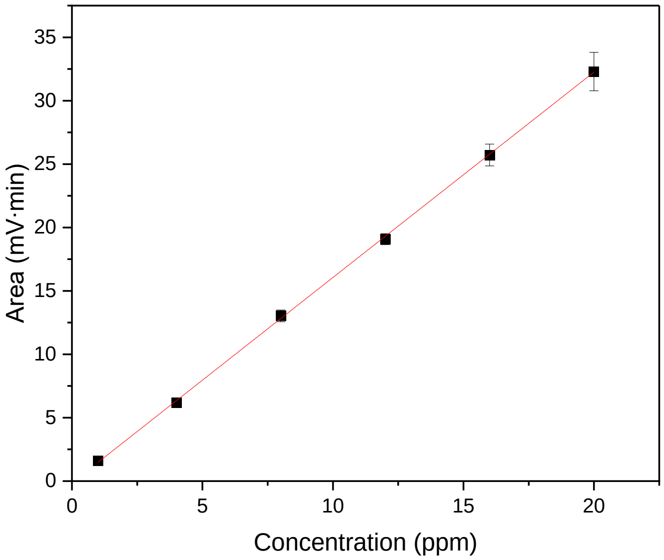
- **Linearity, limit of detection (LD) and limit of quantification (LQ)**

A calibration curve was constructed at five concentration levels in the range of 1-20 ppm from a triplicate analysis (Figure 10a), with the purpose of evaluating the NPOC method developed. The analytical parameters of the calibration curve were obtained by linear regression, in which the equation corresponds to $y = 1.620x – 0.14$, and its angular coefficient is related to the sensitivity of the method to the polymer content present in the samples. From this, a coefficient of determination (R^2) equal to 0.9998 was attained, indicating the adequacy to the linear model.

Intending to assess the linearity of the curve, a statistical F-test was conducted through the Lack of Fit analysis [33]. The result confirms the linearity of the calibration curve in the concentration range studied, since the p-value of 0.97293 is higher than 0.05 for a significance level of 5%. Additional information of this analysis are shown in Appendix 9.1 (Table 12), as well as the linear range of the method, evaluated within polymer concentrations up to 80 ppm in water (Figure 15).

Other figures of merit were also obtained, such as the limit of detection (LOD) and limit of quantification (LOQ) determined as: $LOD = (3 \times s_a)/b$ and $LOQ = (10 \times s_a)/b$, in which s_a corresponds to the standard deviation of the linear coefficient from the calibration curve, and b represents its slope [34]. The values obtained (Figure 10b) attest that the method is suitable for the quantification of PAM-AMPS 1 in water matrix even at low concentration levels (>0.99 ppm).

(a)



(b)

Parameters	Value
R^2	0.9998
LOD / ppm	0.30
LOQ / ppm	0.99
Slope	1.620 ± 0.010
Intercept	-0.14 ± 0.16

Figure 10. (a) Calibration curve obtained from the NPOC method in the concentration range of 1-20 ppm of PAM-AMPS 1 and its respective **(b)** figures of merit.

- **Precision and accuracy**

Precision was determined based on the repeatability of the polyacrylamide quantification in water at three levels of concentration (3, 10 and 18 ppm). The coefficients of variation obtained were less than 5% at all the concentration levels evaluated (Table 6), suggesting a small variability of the measurements for different replicates. Thus, it can be affirmed that the method is precise, given that the maximum value accepted for quantitative methods is 10% [35].

Concerning the relative errors for each analysis, the values obtained were also less than 5% (Table 6), which confers high accuracy to the method developed for the determination of polyacrylamide in water. Furthermore, it is possible to identify a lower relative error for the 10-ppm samples when compared to the other ones, proving that the quantification of samples with concentration near to the middle of the calibration curve provides more accurate results.

Table 6. TOC quantitative analysis of PAM-AMPS 1 in water for six replicates at different concentration levels.

Expected polymer concentration / ppm	Concentration (n = 6) / ppm	Relative Error / %	Coefficient of Variation / %
3	3.1 ± 0.1	4.6	3.0
10	10.1 ± 0.2	0.9	2.1
18	18.3 ± 0.3	1.5	1.5

5.2. Impact of salt content on the quantification of PAM-AMPS by TOC

Back-produced polymers are mostly present in salty waters and depending on the technique and methods applied to determine its concentration, the amount of salt may be a concern. Therefore, two tests were performed aiming to assess whether the salt content present in polymer samples would interfere on the TOC method developed.

As shown in Table 7, no significant interference of the salt content on the quantification of PAM-AMPS 1 was found for samples comprising 1 and 10 wt.% of salt from the synthetic produced water. In fact, the smallest error observed was for the samples with the highest salt content, indicating that the brine did not affect the accuracy of the method. On the other hand, increasing the salt content increased the variability of the results, nevertheless, it should be noted that the coefficient of variation was <5%, despite the amount of salt present in the medium. Therefore, it highlights the advantage of the TOC method regarding the salt interference.

Table 7. Quantification by TOC of PAM-AMPS 1 samples in brine with 1 and 10% of salt content

Salt content / wt.%	Expected polymer concentration / ppm	Concentration (n = 3) / ppm	Relative Error / %	Coefficient of Variation / %
0[a]	10.0	10.1 ± 0.2	0.9	2.1
1	10.0	10.7 ± 0.3	7.0	2.9
10	10.0	9.9 ± 0.4	1.0	4.1

[a] n = 6 replicates.

Despite the satisfactory results, the performance of TOC equipment used may be impaired if extensive analyses of brine samples with high content of salt are conducted. In the long-term, the deposition of salt in the internal parts of the instrument would affect its sensitivity, thus leading to erroneous results. The maximum concentration of salt recommended by Shimadzu is 1,000 mg L^{-1} (*i.e.*, 0.1 wt.%), otherwise samples must be diluted [20]. Other alternatives to mitigate this problem when analyzing samples with a high salt content could be its treatment by dialysis, whose efficiency of the procedure was reported by Carvalho *et al.* [36], or even the use of a device (Shimadzu B-Type Halogen Scrubber) designed for these sorts of matrices, according to Shimadzu [20].

Another concern regarding the salt in the samples and TOC analysis is the presence of carbonates. Although it was not part of the chemical composition of the brine used in this study, it is worth mentioning that the incomplete removal of this specie may impair the carbon measurements (see section 2.3). Therefore, when analyzing polymer samples in brines containing carbonate salts it may be necessary to evaluate the effectiveness of the NPOC method developed, intending to adjust any conditions, if necessary (*e.g.*, acid concentration, sparge time, pH, etc.), thus avoiding erroneous results.

5.3. Influence of hydrolysis on the quantification of PAM-AMPS by TOC and SEC-UV

The main point to be considered when investigating the effect of polymer chemical degradation by hydrolysis concerns the modifications on its structure and further impairment on the methods of quantification. To test this, it was first verified if some hydrolyzed samples had HD significantly different from PAM-AMPS 1 (sample used for obtaining the calibration curve in TOC), to simulate the degradation. This was done by charactering the macromolecules by ^{13}C NMR. The spectrum of PAM-AMPS 1 is reported in Figure 11 along with the attribution of the chemical signals' correspondent to the carbons of the amide, AMPS, and carboxylate groups; the additional spectra obtained are shown in Appendix 9.

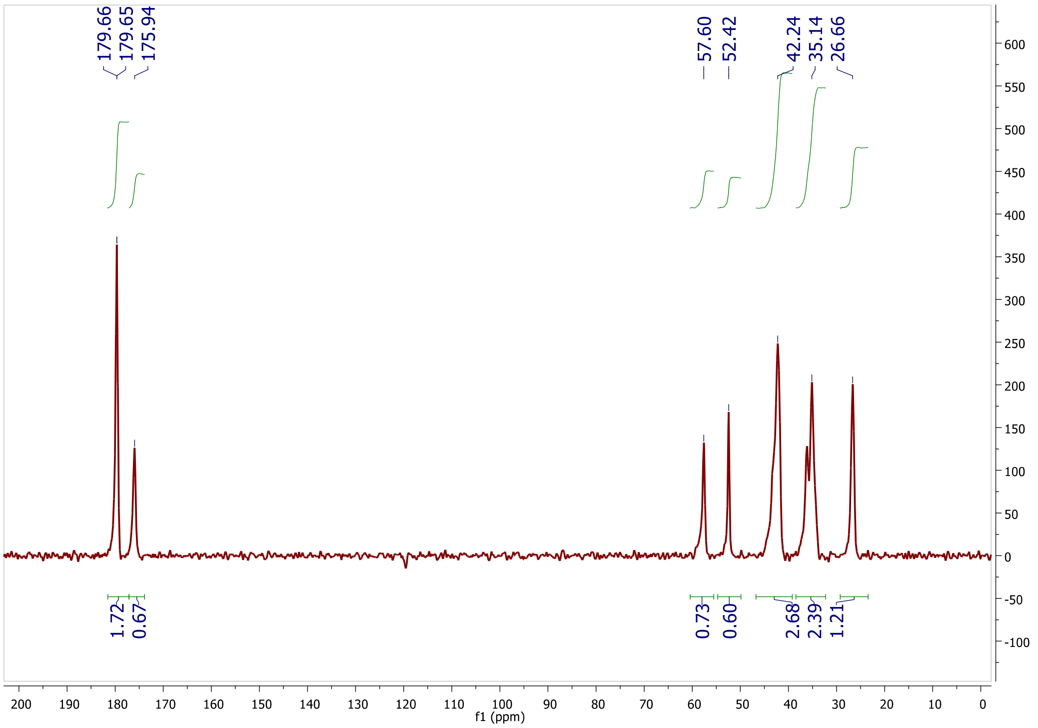


Figure 11. ^{13}C NMR spectrum for PAM-AMPS 1 in D_2O brine.

The HD values were also determined through ATR-FTIR analysis (described in Appendix 9.3) in accordance with the study reported in the literature by Hou and coauthors [22], and the spectra obtained are also presented in Appendix 9.3 (Figure 20). The small differences in the results obtained by ^{13}C NMR and ATR-FTIR (Table 8) confirm the accuracy of the methods. Most importantly, these samples have a HD significantly higher than the polymer used for the construction of the calibration curve in the TOC, while the SD is nearly the same in all cases.

Table 8. Sulfonation and hydrolysis degree (SD and HD, respectively) determined by ^{13}C NMR and ATR-FTIR analyses, and their reference values provided by the manufacturer.

	^{13}C NMR		**ATR-FTIR**	**Reference - SNF**	
Polymer	**SD / %**	**HD / %**	**HD / %**	**SD%**	**HD%**
PAM-AMPS 1	28.0	0.0	1.0	-	-
HPAM-AMPS VLM5	25.9	7.1	5.1	25	5
HPAM-AMPS LM5	24.9	5.0	5.7	25	5
HPAM-AMPS VLM10	23.5	10.0	9.0	25	10
HPAM-AMPS LM10	24.9	9.5	10.2	25	10

Once confirmed the effectiveness of the TOC method for the PAM-AMPS 1 determination, it was evaluated its suitability on the analysis of hydrolyzed polyacrylamides. The results from TOC and SEC-UV analyses of hydrolyzed polymer samples are presented in Figure 12. From a qualitative interpretation of these data, it was observed that the similarity of the TOC results confirmed that not only the hydrolysis itself did not impair the macromolecule quantification, but its magnitude, defined by the HD of polymers, had no interference on it either (considering HD values up to 10%). In contrast, the discrepancy within the SEC-UV results brings up the relevance of this type of degradation as a potential interfering factor on the chromatographic method.

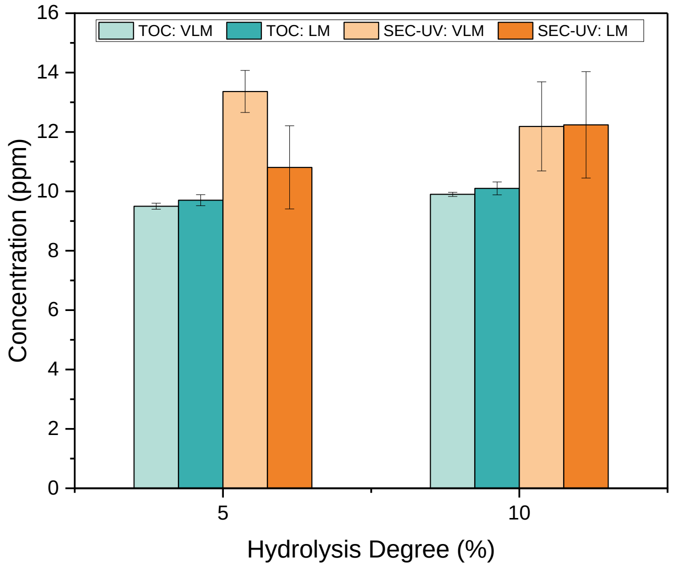


Figure 12. Comparison of the quantification of hydrolyzed polyacrylamide samples (5 and 10%, 10 ppm in water) by TOC and SEC-UV.

As can be seen from the results of the carbon measurements shown in Table 9, the errors obtained were <5% in all cases, which is in accordance with the pre-validation of the method using a non-hydrolyzed polymer. Also, the satisfactory values obtained for the coefficient of variation for TOC indicate the low variability on the analyses performed for different replicates of HPAM-AMPS samples. It suggests the adequacy of the method for such analyses with precision, and, in light of these aspects, it can be assumed that hydrolysis may be not an issue when analyzing the polymers by TOC. These results confirm the expected behavior of TOC, since no changes in the carbon content of the polymer occur after chemical degradation by hydrolysis.

The measurements carried out using the SEC-UV method resulted in the chromatograms showed in Appendix 9.3, with each figure corresponding to an example of an HPAM-AMPS analysis, in which the first peak observed represents the polymer signal and the second one, the aqueous matrix. Regarding the determination of the macromolecule from the SEC-UV analysis, a calibration curve between 5 and 25 ppm of PAM-AMPS 1 was constructed for quantification of the polymers (Appendix 9.5, Figure 25a). The respective figures of merit are reported in Figure 25b, and as observed, the LOQ obtained was higher than the lower concentration level of the curve. It suggests a limitation of the chromatographic method, which may be attributed to its sensitivity for quantitative analysis of extremely low contents of polymer such as 5 ppm. Therefore, under these conditions, quantitative results can only be ensured by the SEC-UV method for analysis of PAM-AMPS 1 at concentrations >7.3 ppm. It must be stressed in all the analysis performed that the polymer concentration was above the LOQ of the method.

From the results presented in Table 9, it can be seen that there were no significant differences in the determination of HPAM-AMPS polymers with 10% HD by SEC-UV. On the other hand, a large variation in the results was observed when the same technique was applied for the analyses of 5% HD polyacrylamides. These results indicate that the SEC-UV method seems to be sensitive to the degree of hydrolysis of the samples, which is undesirable for adequate quantification of back-produced polymers. Additionally, the method resulted in high relative errors and coefficient of variation, with values >10% for both variables in most of the samples analyzed. It is noteworthy that all the concentration values determined by the method were above the expected value (10 ppm), indicating that an increase in the HD resulted in an overestimation in the polymer concentration by SEC-UV. In view of the results presented, it can be stated that the TOC method presented a better response in the quantification of polymers with different HD when compared to SEC-UV, being the best choice for the quantification of this type of samples.

Table 9. TOC and SEC-UV quantitative analyses of hydrolyzed polyacrylamide samples in water (hydrolysis degrees of 5 and 10%).

Hydrolyzed Polymer	**Expected polymer concentration / ppm**	**TOC**			**SEC-UV**		
		Concentration (n=3) / ppm	**Relative Error / %**	**Coefficient of Variation / %**	**Concentration (n=3) / ppm**	**Relative Error / %**	**Coefficient of Variation / %**
HPAM-AMPS VLM5	9.9	9.5 ± 0.1	4.1	1.1	13.4 ± 0.7	34.8	5.3
HPAM-AMPS LM5	10.1	9.7 ± 0.2	3.4	1.9	10.8 ± 1.4	7.1	13.0
HPAM-AMPS VLM10	10.2	9.9 ± 0.1	3.0	0.7	12.2 ± 1.5	19.7	12.3
HPAM-AMPS LM10	10.0	10.1 ± 0.2	0.7	2.1	12.2 ± 1.8	22.4	14.6

Espinosa and coauthors [4] showed that the SEC-UV method had a great response on the quantification of polymers. For a calibration curve in the range of 10 to 50 ppm of sulfonated polyacrylamide, its linearity to the method was indeed proved, which ensured the confidence of the results. However, it is worth mentioning that, in the present work, the choice of using such lower values of polymer concentration for the construction of the calibration curve was due to the intention of analyzing 10 ppm polymer samples, allowing further comparison with TOC results. Considering this, the results obtained led to the conclusion that, under the specific conditions evaluated, TOC method fits better the determination of hydrolyzed polymers in aqueous solutions than SEC-UV.

5.4. Evaluation of the influence of polymer molar mass on the NPOC method

At different stages of polymer flooding, both mechanical and chemical mechanisms of polymer degradation can lead to chain scission, thus resulting in the formation of fragments with varied molar masses. The method used to quantify the polymer at different steps in the process, therefore, needs to be unaffected by the length of the macromolecule. In that sense, the applicability of the TOC method for the determination of polyacrylamides with different molar masses was evaluated in this section.

As shown in Figure 13 and Table 10, the data obtained indicate that the method is adequate for the analysis of sulfonated polyacrylamides with different molar masses. As the errors obtained were <8%, it can be assumed that the polymer concentration values may have good accuracy once determined through TOC analysis under such experimental conditions. In addition, the coefficients of variation lower than 10% highlight the precision of the measurements, indicating a small variation within the replicates analyzed.

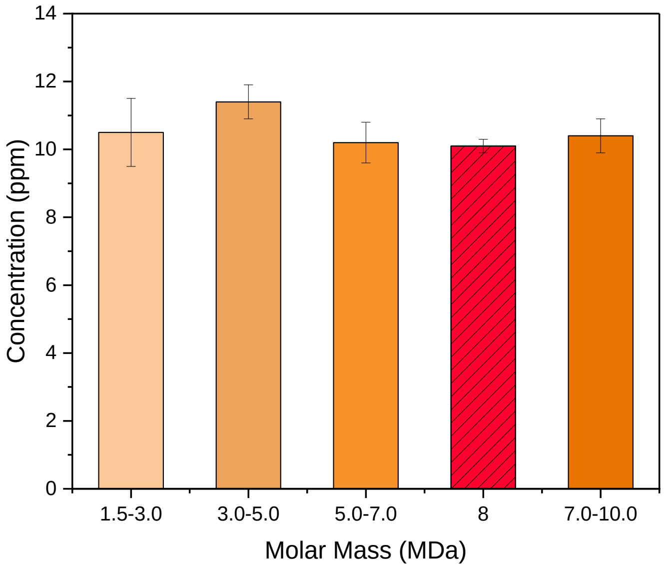


Figure 13. Quantification of polyacrylamide samples with different molar masses. The red column corresponds to six replicates while the others refer to duplicates. The experiments were performed with the polymers dissolved in water.

Table 10. Quantification of polyacrylamide samples (10 ppm in water) with different molar masses.

Molar Mass / MDa	Expected polymer concentration / ppm	Concentration (n = 2) / ppm	Relative Error / %	Coefficient of Variation / %
1.5-3.0	9.9	10.5 ± 1.0	6.1	9.2
3.0-5.0	10.5	11.4 ± 0.5	7.8	4.4
5.0-7.0	10.0	10.2 ± 0.6	1.5	5.6
8.0[a]	10.0	10.1 ± 0.2	0.9	2.1
7.0-10.0	10.1	10.4 ± 0.5	3.0	4.8

[a] n = 6 replicates.

These results proved the great sensitivity of the TOC method regarding the quantification of polyacrylamide with different chain lengths. It can also be linked to the studies concerning other forms of chemical degradation presented in this work in sections 5.3 (hydrolysis) and 5.5 (Fe^{2+}/O_2 reaction). In the former, small changes in the molar mass of the polymer are expected from the chemical changes caused in the amide groups of the macromolecules after hydrolysis, while more significant variations in molar mass are found in the latter, as scission of the main chain (backbone) occurs from the radical reaction with iron.

For example, considering a hypothetical PAM-AMPS with one hundred repetition units, in which amide and AMPS groups mass contributions corresponds, respectively, to 75% and 25%, the molar mass of this polymer would be 11,063.7 $g\cdot mol^{-1}$. In this context, if the macromolecule was chemically degraded by hydrolysis only in the acrylamide portion and presented a final HD of 10%, its molar mass would slightly increase to 11,223.5 g·mol^{-1}. Therefore, it proves that even a small modification in the chemical composition of the polymers is sufficient to provide changes on its molar mass. Hence, degradation at higher extents can have remarkable effects not only on the molar mass of the polymer, but also on their physicochemical properties since the viscosity of the samples may be affected. Nonetheless, regardless of the type of degradation, it is of paramount importance to have a method, such as the one developed in this work, for accurate and precise quantification of polyacrylamide copolymers with different molar masses.

5.5. Effect of chemical degradation by Fe^{2+}/O_2 on the determination of PAM-AMPS by TOC

Prior to the TOC analysis, rheological measurements were carried out to verify if the degradation of PAM-AMPS 1 with iron occurred. For this, non-degraded and degraded samples, in the absence and presence of Fe^{2+}/O_2, respectively, had their viscosity measured. It was observed that the non-degraded polyacrylamide solution behaved as a non-newtonian fluid, as its viscosity decreased with increasing shear rate (Figure 14). Similar shear-thinning behavior was reported by Rahimi and Dehaghani [37] for the same type of a sulfonated polyacrylamide sample analyzed at 10-200 s^{-1}, and under equivalent experimental conditions (25 °C and 1,000 ppm of polymer).

The rheological analyses of the solutions were also performed after the reaction of PAM-AMPS 1 with ferrous ion and oxygen for 48 and 72 h, aiming to evaluate the occurrence of polymer degradation supposedly by chain scission. In Figure 14, an expressive loss in the viscosity could be observed considering the marked change in the flow curves, thus confirming the polymer chemical degradation. Under the conditions used (20 ppm of Fe^{2+}, pH 6 and continuous air bubbling), it can be assumed that complete degradation probably occurs within the first 48 h, as no significant differences in the rheological behavior were identified after this period (Figure 14). Therefore, these results indicate that this procedure could be used to evaluate the degradation effect by Fe^{2+}/O_2 on the polymer quantification through the TOC method.

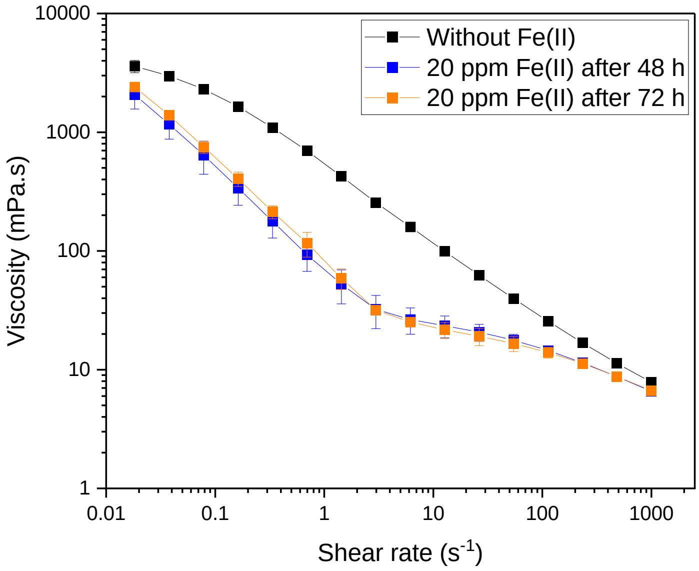


Figure 14. Flow-curves of PAM-AMPS 1 samples (1,000 ppm) before and after the reaction with 20 ppm of Fe(II) in the presence of O_2 for 48 and 72 h.

Although the investigation of how the oxidative degradation of polyacrylamides occurs is beyond the scope of this work, it is worth mentioning some particularities about it. Ramsden and McKay [8] identified a similar behavior through the analysis of the viscosity of polymer samples with the same amount of Fe^{2+} at ambient O_2 conditions for a non-sulfonated polyacrylamide under fixed values of pH and at a higher polymer concentration (0.5%). The authors reported that the degradation effects were more pronounced at pHs 7 and 6, where a greater loss in the viscosity was observed, and within this pH range there were almost no changes in the extent of degradation. Additionally, mild degradation was identified for pH values lower than 4 and higher than 7. In this work no significant changes on the pH of samples were observed from the qualitative measurements, as the pH value remained around 6.

According to the literature, the autoxidation reaction of ferrous ion in the presence of dissolved oxygen is reported to provide changes in the pH of the solutions [8]. Since from the experiments carried out no changes in the pH of the polymer samples were observed, two aspects can be considered: first, the kinetics of this reaction may be slow, considering the conditions used, and thus a more pronounced variation in the pH would take more days to occur; second, there was not enough O_2 in the medium to induce the complete autoxidation of Fe^{2+}. In either case, the concentration of ferrous ion (20 ppm) is not going to be considered as a potential problem in this context once it the degradation of polymer with 20 ppm of Fe^{2+} was confirmed.

As previously mentioned, polyacrylamides may be attacked by free radicals at different regions of its chemical structure, and as different sites would result in different reaction products, this type of degradation is challenging regarding the proper quantification of each product. Therefore, intending to evaluate the effect of this chemical degradation on the macromolecule quantification, the degraded polymer samples were analyzed using the TOC method after dilution to 10 ppm. It can be observed in Table 11 that the extent of polymer degradation did not influence on carbon measurements, thus not impairing on the polyacrylamide quantification. For 48 and 72 h of reaction time, the relative error of the analyses was less than 7%, suggesting a good response to the method.

As no carbon source is lost during the reaction, for example, by the production of gases such as CO_2, and all subproducts remain in solution, this type of polymer degradation is not expected to impair the determination of the macromolecule. However, some by-products with low volatility, *e.g.* ketone and aldehyde, can be formed [31]. These classes of compounds can be lost during the purge step of the NPOC method, thus affecting quantification. Since the observed results demonstrated that the TOC method was not affected by the degradation reaction, two hypotheses can be raised: 1) the conditions (polymer type, concentration, temperature, etc.) did not lead to the formation of volatile products, or 2) such compounds were indeed formed, but in very small amounts, insufficient to cause any interference in the method. Despite its relevance, further investigation on the subject is out of the scope of this work.

Table 11. Quantification of 10 ppm PAM-AMPS 1 samples after the reaction with $Fe(II)/O_2$ for 48 and 72 h.

Fe(II) reaction time / h	**Concentration (n = 2) / ppm**	**Relative Error / %**
48	9.3 ± 0.2	6.8
72	10.2 ± 0.6	1.6

6 CONCLUSIONS

The quantification of back-produced polyacrylamide may be not an easy task mainly due the degradation of the macromolecule during the EOR processes, besides the matrix complexity. In this study a quantitative method was developed based on carbon measurements by TOC analyses of intact polymer samples of PAM-AMPS 1. The choice for using such technique and equipment was made considering that it demands a short time for the conduction of the tests, is easy to operate and also requires low consumption of reagents, which is economically favorable. From the pre-validation of the developed method, the satisfactory data obtained (relative errors and coefficients of variation <5%) proved its suitability for the analysis of the polymer in aqueous matrices, also confirming its efficacy in providing accurate concentration values of the analyte.

Considering the context of EOR processes, it is known the polyacrylamide copolymers can be modified through the different steps until being analyzed in the produced water. In that sense, the TOC method developed for the intact polymer was evaluated regarding the influence of salinity, molar mass and two types of degradation. Based on the results obtained, it has been confirmed that the salt content does not affect the quantification of the polymer. The method showed a great response, with the determined concentration values agreeing with the expected ones within relative errors in the range of 1 to 7%. These observations indicate the good potential of the method for analyzing back produced polymer in brine from oilfields. However, the TOC equipment used to perform the analysis possesses a limitation regarding the salt content, and as mentioned, some preventive actions must be taken to avoid damage to the instrument after extensive analyses of polymer samples in brine.

Regarding the molar mass of the polymers and the degradation mechanisms evaluated (by hydrolysis, considering HD values up to 10%, and reaction with Fe^{2+}/O_2), it was proved that these aspects did not impair the TOC analyses either. As the errors obtained in all cases were lower than 8%, it indicates that the quantification of the macromolecule in aqueous systems can be achieved with good accuracy and in a relative short time, since the equipment and technique provide rapid results.

Supported by the results found in this work, one could consider the quantification of polyacrylamide in wastewater from oilfield using the TOC method. As shown, it suggests that under the conditions tested, this method has a promising application considering the potential interfering factors evaluated, such as matrix salinity, changes in the polymer molar mass and its chemical degradation.

7 FUTURE INVESTIGATIONS

As future investigations to complement the present work it is recommended to:

- Evaluate if dialysis affects the TOC method and if it is suitable for eliminating potential interferences, specifically carbon sources besides the polymer, in a complex polymer sample with a matrix similar to that of produced water. These assessments are critical in determining the validity of the TOC method for analyzing real samples from oilfield processes.
- Test other conditions for the degradation reaction of polyacrylamide with Fe^{2+}/O_2 while analyzing the sample by rheology and TOC. For example, it could be interesting to assess the behavior of the polymer under different conditions by controlling the concentration of dissolved O_2 in the sample throughout the procedure, varying the temperature, and extending the reaction time to longer periods (>72 h).
- Characterize by ATR-FTIR the samples degraded by Fe^{2+}/O_2, once it could provide some useful additional information about this mechanism of chemical degradation, for instance, shedding light on the subproducts formed in the reaction. Additionally, analyze the same polymer samples by SEC-UV and mass spectrometry could also contribute to a better understanding of the reaction with polyacrylamide.

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9 APPENDIX

9.1. Linear range TOC and F-test Lack of Fit

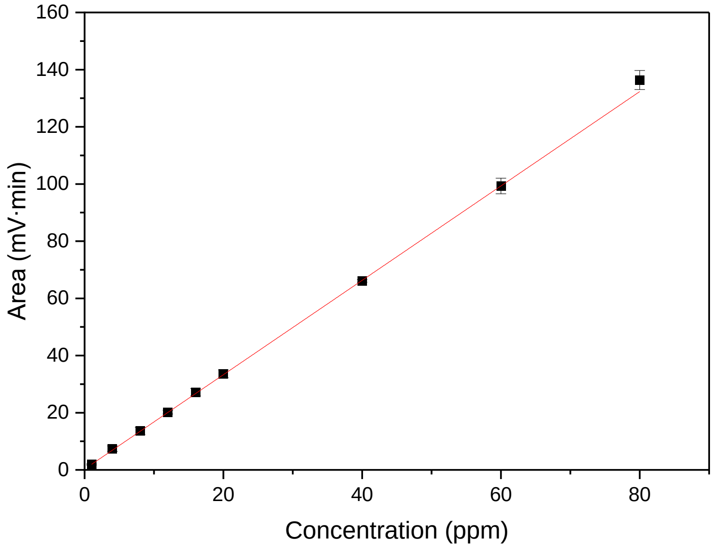


Figure 15. Evaluation of the linear range for the NPOC method ($R^2 = 0.9999$).

Table 12. F-Test Lack of Fit for the TOC calibration curve obtained through the NPOC method.

	Degrees of Freedom (DF)	Sum of Squares	Mean Square	F Value	Prob > F
Lack of Fit	4	0.10918	0.0273	0.11942	0.97293
Pure Error	12	2.74285	0.22857		
Error	16	2.85203			

9.2. ^{13}C NMR spectra

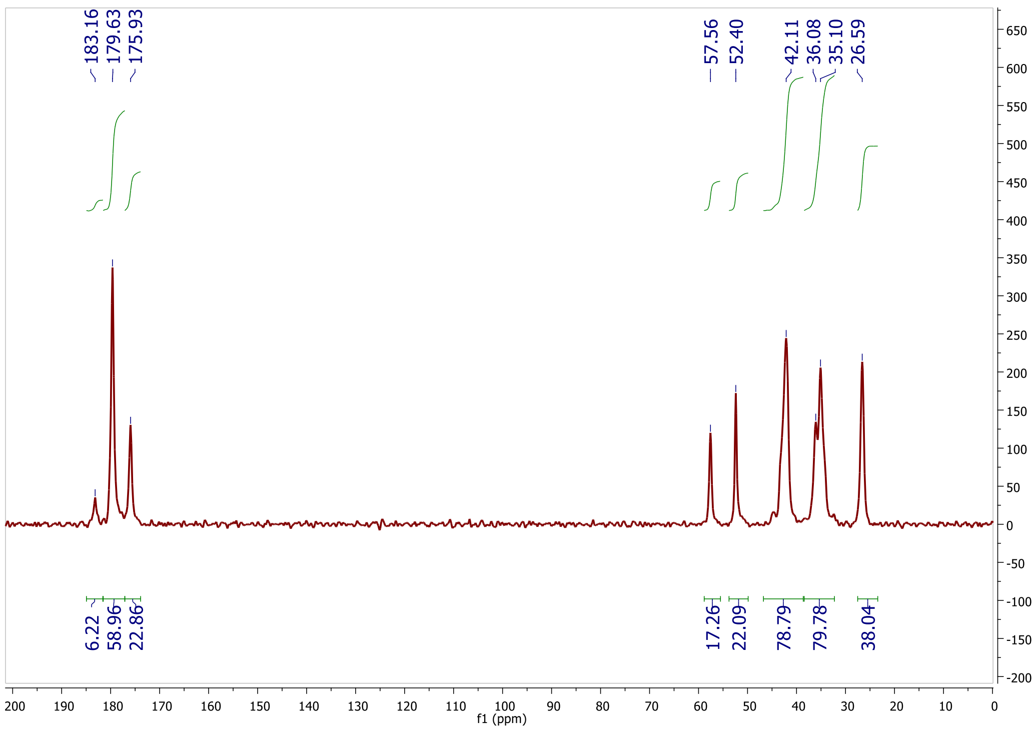


Figure 16. ^{13}C NMR spectrum for HPAM-AMPS VLM5 in D_2O brine. The chemical signals correspondent to amide, AMPS and carboxylate groups were respectively identified in the regions of 179.63 ppm, 175.93 ppm and 183.16 ppm.

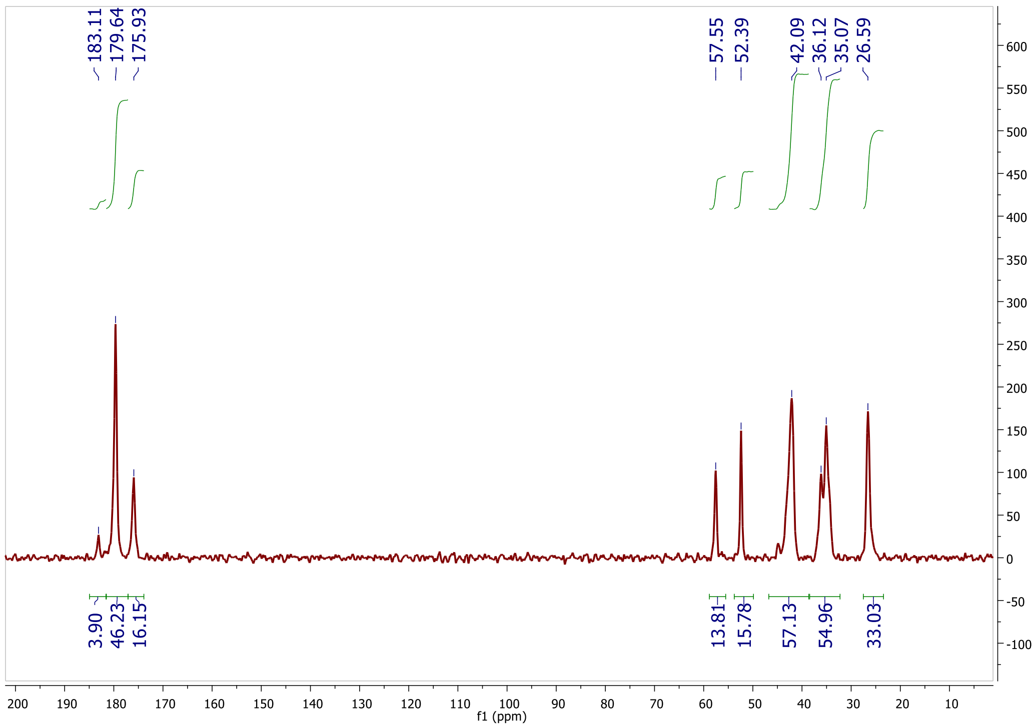


Figure 17. ^{13}C NMR spectrum for HPAM-AMPS LM5 in D_2O brine. The chemical signals correspondent to amide, AMPS and carboxylate groups were respectively identified in the regions of 179.64 ppm, 175.93 ppm and 183.11 ppm.

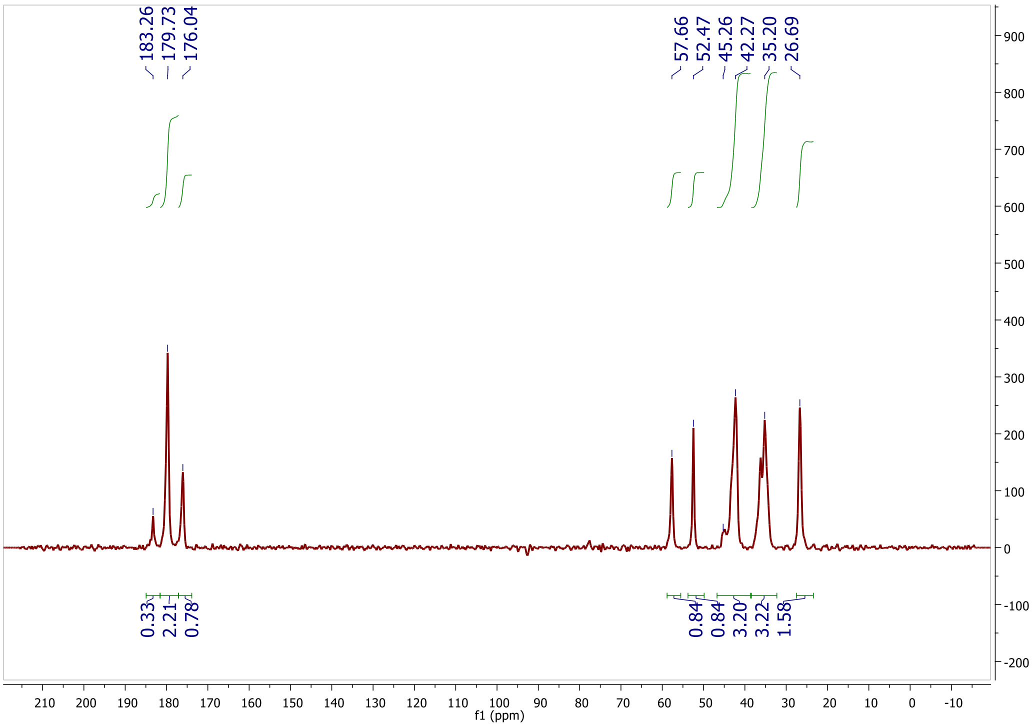


Figure 18. ^{13}C NMR spectrum for HPAM-AMPS VLM10 in D_2O brine. The chemical signals correspondent to amide, AMPS and carboxylate groups were respectively identified in the regions of 179.73 ppm, 176.04 ppm and 183.26 ppm.

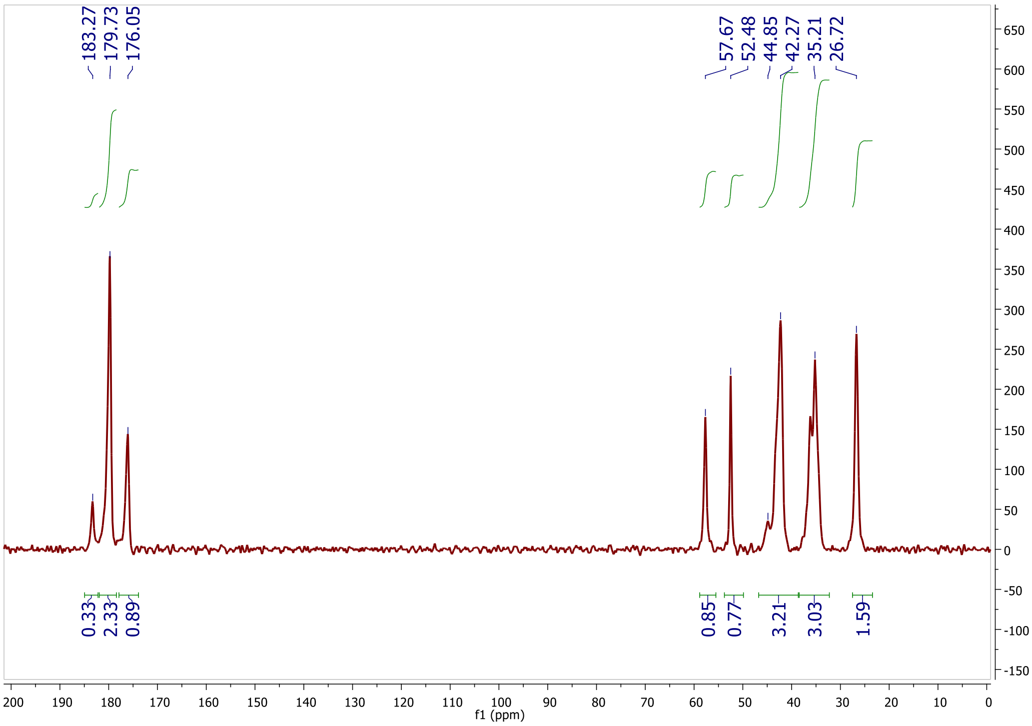


Figure 19. ^{13}C NMR spectrum for HPAM-AMPS LM10 in D_2O brine. The chemical signals correspondent to amide, AMPS and carboxylate groups were respectively identified in the regions of 179.73 ppm, 176.05 ppm and 183.27 ppm.

9.3. ATR-FTIR spectra and determination of the HD of polymers

Considering the data obtained from the ATR-FTIR spectra of PAM-AMPS 1 and the four types of HPAM-AMPS polymers (Figure 20), the HD of each macromolecule was determined similarly as reported by Hou, Han and Fuseni [22]. As the HD of the polymers increase, it is possible to observe a change in the spectra in the intensity of the peaks corresponding to the carbonyl from the amide (1652 cm^{-1}) and carboxylate (1558 cm^{-1}) groups formed after hydrolysis. Therefore, considering the intensity of both signals, the ratio between them was calculated and used to determine the HD through a calibration curve constructed with standards of different hydrolysis degrees.

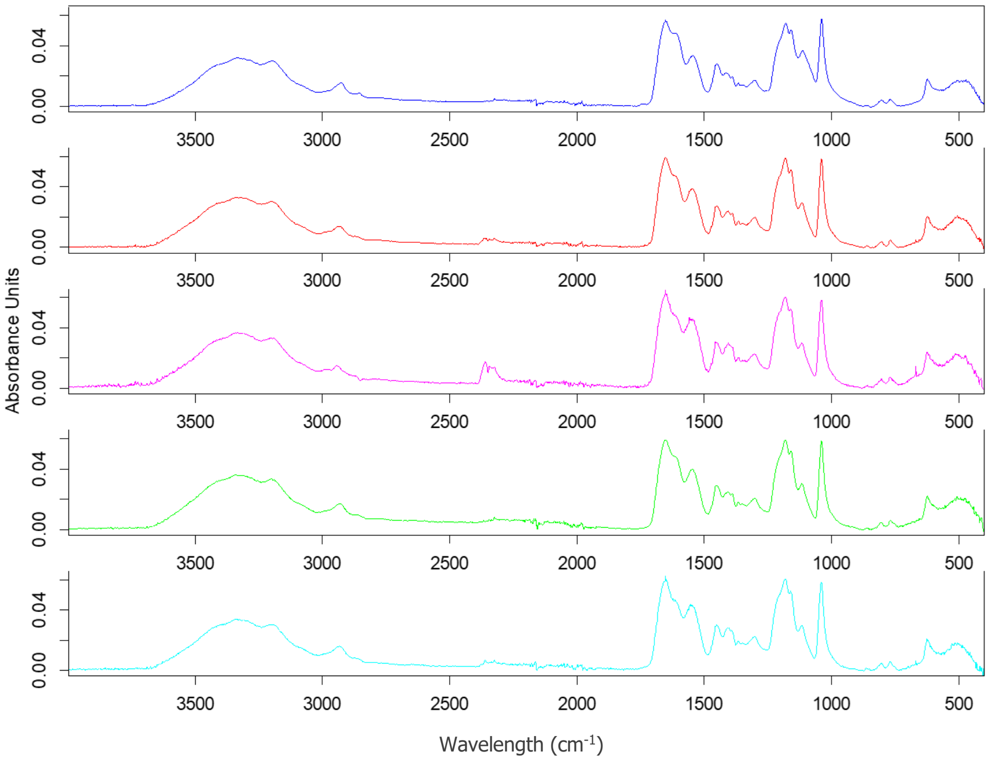


Figure 20. Spectra obtained from ATR-FTIR measurements. From the bottom to the top, the respective polymers are PAM-AMPS 1, HPAM-AMPS LM5, HPAM-AMPS LM10, HPAM-AMPS VLM5 and HPAM-AMPS VLM10.

9.4. SEC-UV chromatograms

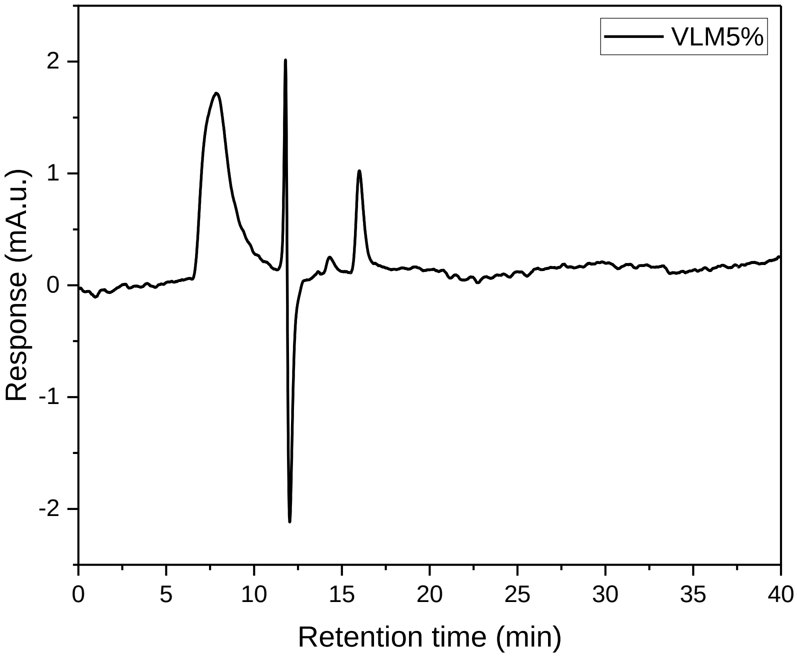


Figure 21. Representation of the chromatogram obtained from SEC-UV method for HPAM-AMPS VLM5. The first peak corresponds to the polymer.

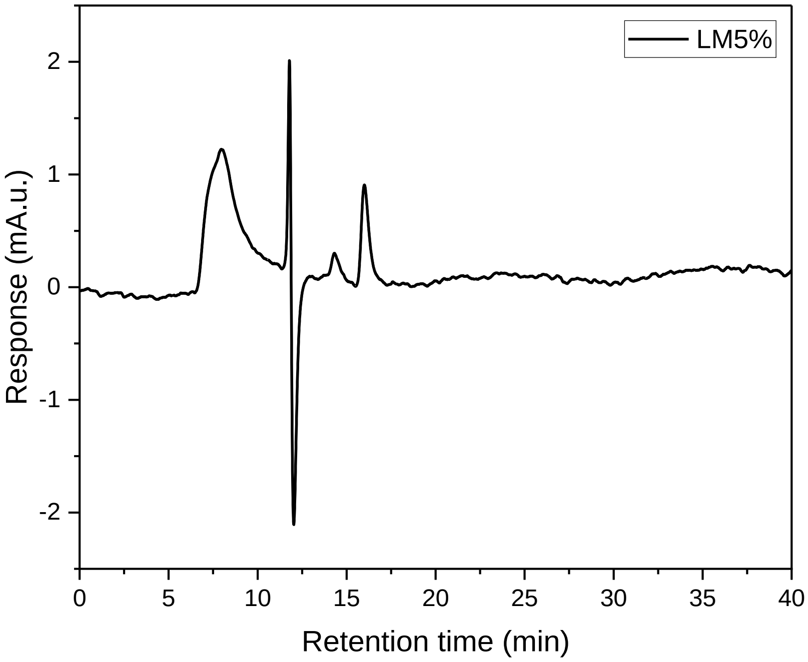


Figure 22. Representation of the chromatogram obtained from SEC-UV method for HPAM-AMPS LM5. The first peak corresponds to the polymer.

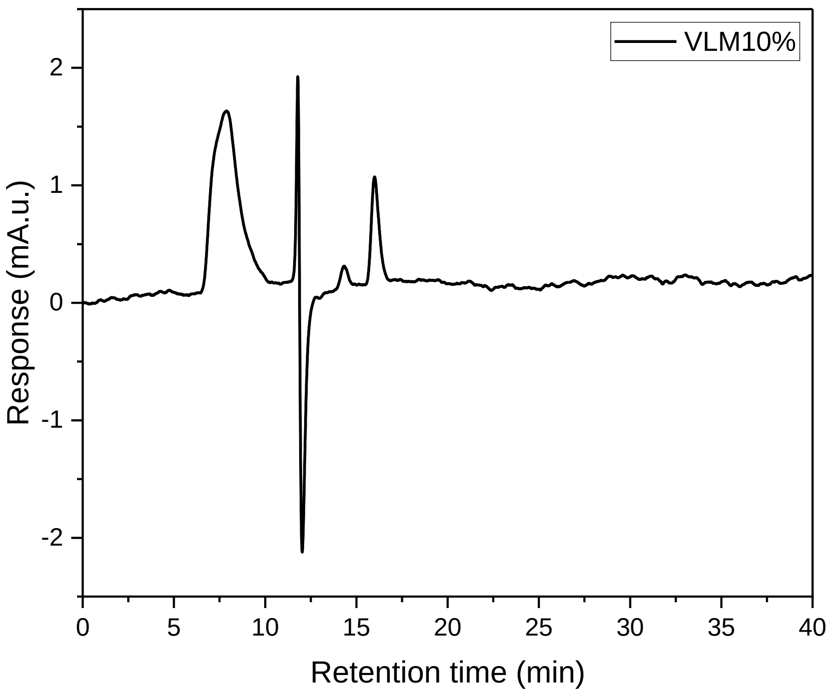


Figure 23. Representation of the chromatogram obtained from SEC-UV method for HPAM-AMPS VLM10. The first peak corresponds to the polymer.

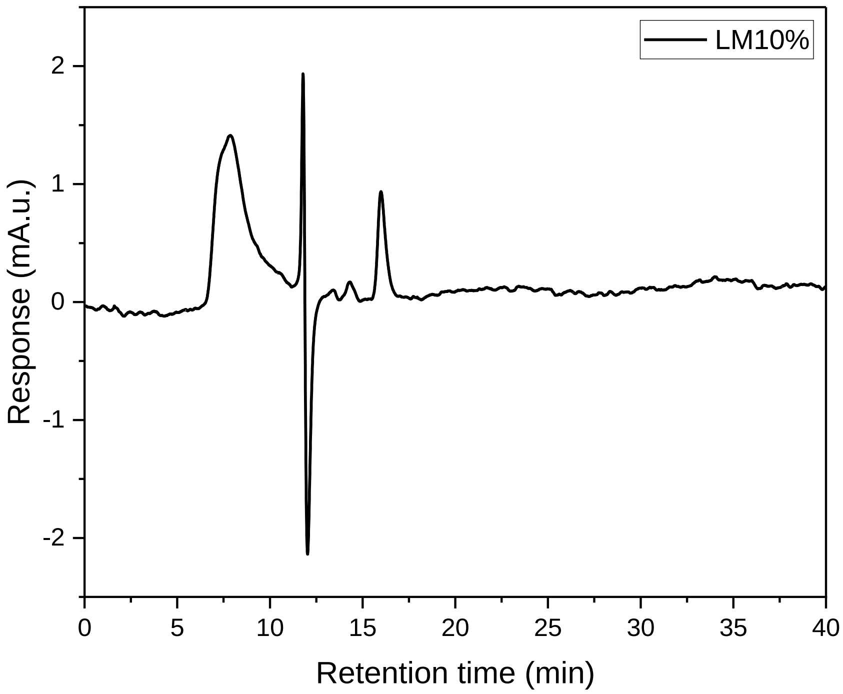
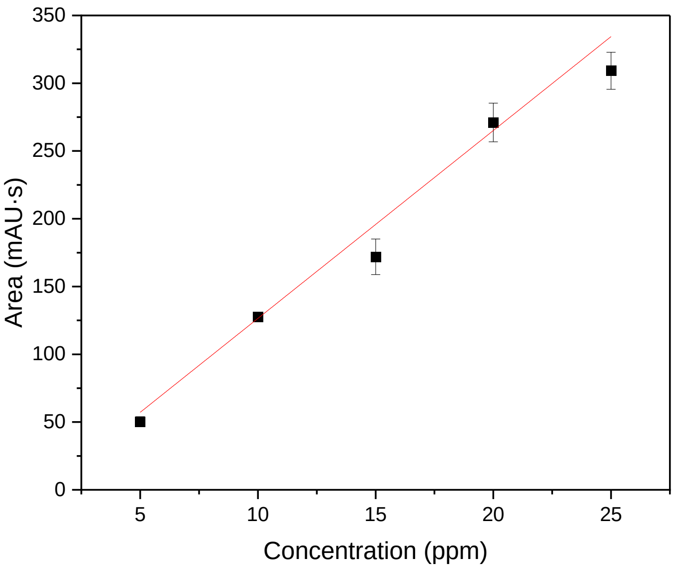


Figure 24. Representation of the chromatogram obtained from SEC-UV method for HPAM-AMPS LM10. The first peak corresponds to the polymer.

9.5. Analytical parameter of the SEC-UV method: linearity, limit of detection (LOD), limit of quantification (LOQ)

(a)

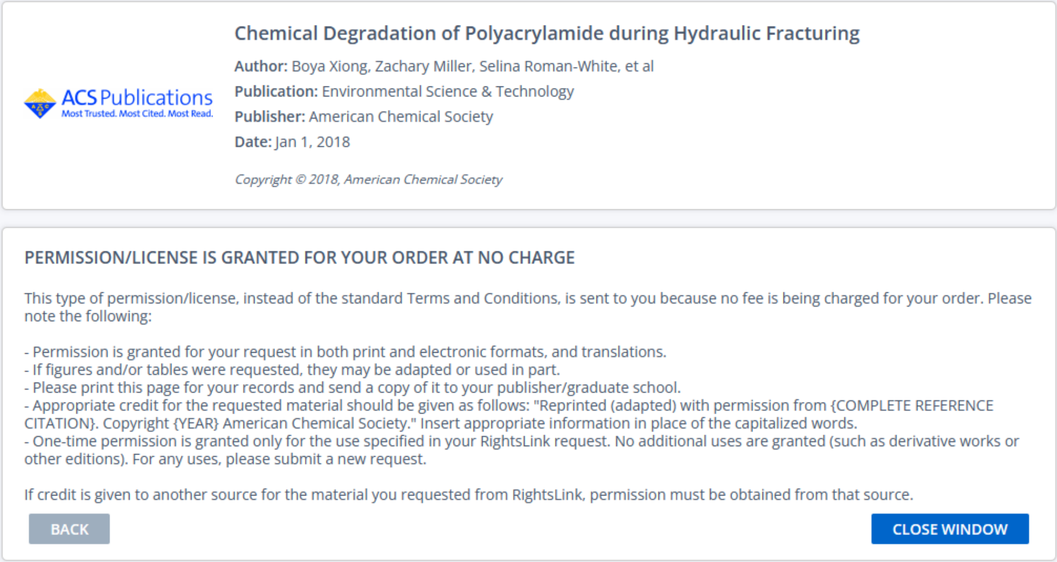


(b)

Parameters	**Value**
R^2	0.9841
LOD / ppm	2.20
LOQ / ppm	7.34
Slope	13.86 ± 1.02
Intercept	-12.15 ± 10.17

Figure 25. (a) SEC-UV calibration curve in the range of 5 to 25 ppm of PAM-AMPS 1 in water and its **(b)** figures of merit.

10 ANNEX



Chemical Degradation of Polyacrylamide during Hydraulic Fracturing

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Figure 26. Permission for using the adapted figure reprinted as Figure 8 in this work.