# FTIR Method for PRAESTOL™ A3040L Analysis in Surface Waters

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PRAESTOL<sup>™</sup> products series are new organic flocculating agents designed for solid-liquid separation, being used in industrial water and wastewater treatment. Some products from this series are even used for drinking water purification. Given the fact that the environmental fate of the copolymers is largely unknown and the high toxicity of its precursors, acrylamide and sodium acrylate, the development of analytical methods for Praestol<sup>™</sup> content analysis in effluents is appropriate. This work focuses on using a Fourier Transform Infrared Spectrometric (FTIR) method for the determination of one product from these series, namely Praestol<sup>™</sup> A3040L from water samples. After liquid-liquid extraction, the Praestol<sup>™</sup> content is obtained from the IR spectra by multiple peaks data analysis. The developed method is especially suited for the routine monitoring of effluents from the industrial units using this product and allows some basic interference detection.

Keywords: quantitative FTIR, Praestol<sup>™</sup> content in water, petroleum distillates, aqueous emulsion

The Praestol<sup>™</sup> products series are synthetic polyelectrolytes of high molecular weight based on polyacrylamide copolymer emulsions. The flocculating property of Praestol<sup>™</sup> products is due to the presence in their composition of different reactive groups which in aqueous solution have a high affinity for the surface of the colloidal particles suspended in aqueous or sludge systems making them suitable for all kinds of practical applications in solid-liquid separation processes. The interactions mechanism with solid particles may be different depending on the treated suspension characteristics and on the type of the polyelectrolytes ionic charge. The mechanism may be based either on the formation of hydrogen bonds in the case of non-ionic polymers, or on the electrostatic interactions with the surface charged colloidal particles for the anionic and cationic flocculating agents. Because of the electrical charges in the polymer chains, the anionic and cationic polyelectrolytes have the capacity to easily adsorb different suspended elementary particles, promoting the destabilization and aggregation of suspended matter, thus facilitating the gravitational sedimentation and filtration processes. Therefore, Praestol<sup>™</sup> products can be used in industrial water and wastewater treatment, sludge dewatering, sludge treatment in waterworks and nutrients removal from different wastewaters [1-12].

This work is aimed to the development of a new FTIR method for Praestol<sup>TM</sup> A3040L content analysis in water, with applicability in industrial effluents quality monitoring from water treatment installations.

The A3040L flocculant is a moderately anionic polyelectrolyte with an average molecular weight, containing acrylamide - sodium acrylate copolymers, ethoxylated alcohols and *hydrotreated light petroleum distillates* as an aqueous emulsion. This flocculant presents itself as a milky white liquid, slowly but completely miscible with water, being mainly used as an adjunct to coagulation of mineral and hydroxide solid particles and colloids from various types of waters and water slurries, thus most suitable for the clarification of industrial water from the treatment of mining raw materials, the metallurgical and the chemical industry. Also it can be used in a range of application for the surface, ground waters and various types of wastewaters treatment, in conjunction with hydroxide forming coagulants, especially with ferric chloride [1, 13].

According to Material Safety Data Sheet ID WT-149B, A3040L has an acute toxicity LC50 after 48 hours of 11.0 ppm on *Ceriodaphnia dubia* [13], and its NOEC is expected to be lower still.

## Experimental part

Reagents and materials

The Praestol<sup>TM</sup> A3040L reagent was supplied from Ashland, Germany. Hydrochloric acid p.a. (Sigma-Aldrich) was used for aqueous solutions *p*H adjustment. Carbon tetrachloride >99.9 % (J.T.Baker) was used as FTIR solvent. Florisil<sup>TM</sup> and anhydrous sodium sulphate packed glass columns were used for organic extract purification. All analytical solutions were prepared using double-distilled water. Spiked samples were prepared with natural river water.

#### Apparatus

Gravimetric measurements were performed using a Kern 770-14 analytical balance. Volumetric measurements were performed using Class A laboratory glassware. Concentrated A3040L solutions were homogenized using a Heidolph MR 3004 magnetic stirrer and a PTFE coated magnetic bar. *p*H measurements were carried out using a Mettler Toledo MP125 pH meter. The absorbent materials were thermally conditioned using a Nabertherm P320 oven. FTIR spectra were obtained using a Jasco FT/IR 4100 spectrometer with potassium bromide cell (Specac OmniCell<sup>™</sup> System, 1.00 mm PTFE spacer), 10 mm and 40 mm IR quartz transmission cells. FTIR spectra acquisition, conversion and integration were carried out using Jasco Spectra Manager<sup>™</sup> software suite version 2.

## Preparation of standard solutions

Due to its high viscosity and pronounced adhesion phenomena on glass surfaces, A3040L concentrated solutions, prepared using pipettes or other volumetric means of dosing the required amount of product have an

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unacceptable uncertainty caused by the impossibility of quantitative transference of the measured volume. This impediment was overcome by using the following gravimetric method for the preparation of the concentrated solutions with a reasonable uncertainty. The required A3040L mass (about 0.1 g) was introduced drop by drop on the bottom of a previously dried 100 mL Class A volumetric flask tarred on an analytical balance, using a suitable capillary glass Pasteur pipet. The volumetric flask containing the desired product quantity was slowly brought to volume with double-distilled water, avoiding the formation of foam, after which a suitable PTFE coated magnetic bar was introduced and the solution was homogenized on a magnetic stirrer for a few hours until the entire product was thoroughly dispersed.

All glassware that came into contact with A3040L should be thoroughly cleaned with detergent and tap water, filled with an oxidizing solution (sulfochromic mixture) for at least 30 min., and finally rinsed with tap and double-distilled water.

#### **Results and discussions**

Praestol<sup>™</sup> A3040L is a multicomponent copolymer mixture containing, among others, acrylamide – sodium acrylate copolymers, *distilled oil fractions* and ethoxylated alcohols [13].

Considering its known components, the product could be theoretically detected by UV-Vis-NIR [2] and FTIR spectrometry, gas chromatography (GC) [3], liquid chromatography (HPLC) and liquid chromatography coupled with mass spectrometry (LC-MS). Electrochemical methods (potentiometric [4], cyclic voltammetry and differential pulse voltammetry) could also be considered given the electronically unbalanced functionalized groups in the polymer chains. This paper covers the FTIR analysis possibilities of the product.

The first FTIR tests were carried out on A3040L solutions made in double-distilled water with concentrations ranging from 0.5 to 10 mg·L<sup>-1</sup> in respect to the aqueous solution. The preliminary tests comprised a liquid-liquid extraction with CCl<sub>4</sub> followed by organic extract FTIR spectra acquisition using 10 mm quartz cells (fig. 1), with the objective of observing the presence of any concentration dependent absorption bands (fig. 2).

As it can be observed from figure 1, the wavenumber range allowed by the use of IR quartz cells is contained between 7800 – 2400 cm<sup>-1</sup>. The absorption bands observed from the empty KBr cell are caused by traces of mineral oil used for the protection of the salt windows.

The next step of the method development process was the insertion in the sample treatment stages of steps designed to limit the potential interferences from other natural water samples constituents. The subsequent test evaluated the aqueous pH influence on extraction step efficiency (fig. 3) and the influence of various adsorbent materials for organic extract purification (fig. 4).

The basic *p*H solution developed a high degree of emulsification in the extraction step and subsequently, the intensity of the observed absorption bands decreased. The adsorption bands of the spectra at neutral and acidic pH have similar intensities. The emulsification phenomenon was greatly reduced at acidic *p*H. The specific absorbent used for the organic extract purification have a subtle but detectable influence on the spectra (in respect with the various peak ratios) showed in figure 4 denoting a slightly different degree of polar organic compound separation.

The most reproducible results were obtained using the following sample pre-treatment procedure:

- 1 dm<sup>3</sup> of aqueous sample was acidified with 1 cm<sup>3</sup> of conc. HCl (the extraction *p*H must be lower than 2);

- the acidified aqueous sample  $(1 \text{ dm}^3)$  was extracted with 25 cm<sup>3</sup> of CCl<sub>4</sub>, allowing sufficient times for homogenization and organic extract separation;

- the obtained clear extract was collected in a glass stoppered flask (if the organic extract is highly emulsified, 0.5-1 g of anhydrous sodium sulphate were added in the flask);

- the organic extract was passed through the purification glass column containing 2 g of Florisil<sup>M</sup> and 2 g of anhydrous sodium sulphate at the top (one column per sample) and the resulted efluent was collected in a capped glass ampoule.







The acidification is required to promote the extraction of nonpolar organic compounds and it seemed to reduce the organic extract emulsification phenomena observed for A3040L aqueous solutions. The purification step removes the water and polar traces from the organic extract, reducing the possibility of interference from polar compounds as surfactants, alcohols, phenols and so on.

The organic extract FTIR spectra must be acquired versus a baseline obtained from a blank organic sample obtained following all the steps of the sample pre-treatment procedure with 1 dm<sup>3</sup> of doubled-distilled water.

The organic extract qualitative FTIR analysis was carried out using an OmniCell<sup>™</sup> System (1 mm optical path) with KBr salt windows and confirmed the assumption that the analysed organic extract contained only aliphatic hydrocarbons (fig. 5).

Because of the lack of quantitative relevant information provided by the spectra under 2200 cm<sup>-1</sup> in this case and the added costs and difficulty in using KBr cells for routine analyses, for the next experiments IR quartz cells were used, with the added benefit of durability and longer optical paths (10 mm and 40 mm) which improved the method detection limit.

Figure 6 shows the obtained spectra for 5 calibration solutions with concentrations ranging from 1 to 9 mg·L<sup>-1</sup> in respect to the aqueous solution. The spectra were obtained using a 10 mm quartz cell and converted from transmittance into absorbance units to ensure an adequate correlation with the samples concentration.

The main challenge of the proposed analysis method consists in assuring adequate interferences detection by data evaluation, since all aliphatic hydrocarbons have, in different degrees, adsorption bands in 3000 – 2800 cm<sup>-1</sup> range attributed to various C-H bonds [14]. The analytical signal derived from the developed absorption bands can only be analysed together, following some boundary conditions. One of the ways to achieve A3040L signal interferences detection is to implement and calibrate a multivariate approach needing up to hundreds of known samples analysed for a proper use [14].

The A3040L analytical signal specificity in the 3000 -2800 cm<sup>-1</sup> range is constituted by the ratios between the magnitude of each peak (table 1), the absence of supplementary peaks and the wavenumber of the peaks. The simplest way to assure a minimum detection of interferences is to visualize the unknown spectra (if other peaks are present, the method cannot successfully separate the interference and a more advance separation is needed, either by GC [3] or LC), verify the peak ratios against the calibration and validations peak ratios (table 1), extract the analytical signal from the 4 peaks (height or area), interpolate each peak's signal on the corresponding calibration function (fig. 7) and statistically compare the 4 resulted concentrations. If the peak ratios or the calculated 4 concentrations deviate from the mean in an amount corresponding just to the instrumental noise, the specific hydrocarbons mixture present is sufficiently similar to the mixture contained by A3040L and the analyte is



Fig. 6. A3040L absorbance – converted calibration spectra (10 mm quartz cell)



Fig. 7. Linear dependencies between peak areas and concentrations





Table 3

A3040L AND DIESEL FUEL SPIKED SAMPLES CONCENTRATIONS

|         | P1   | <b>P</b> 2 | P3   | P4   | Average | RSD   |
|---------|------|------------|------|------|---------|-------|
| BDW     | 3.24 | 3.21       | 3.18 | 3.23 | 3.21    | 0.8%  |
| River 1 | 3.12 | 3.12       | 3.07 | 3.17 | 3.12    | 1.3%  |
| River 2 | 3.29 | 3.27       | 3.24 | 3.31 | 3.28    | 0.9%  |
| Diesel  | 0.66 | 1.41       | 0.48 | 1.92 | 1.12    | 59.6% |

successfully identified and quantified in the unknown sample.

This analysis method was tested with natural river water spiked with A3040L and diesel fuel (fig. 8).

The peak ratios of the A3040L spiked samples (table 2) have values in the ranges defined by the average  $\pm$  standard deviation of the calibration spectra (table 1) whereas the peak ratios for the diesel fuel spiked sample spectra are clearly different. Also, the 4 concentrations (table 3) calculated for each A3040L spiked sample are similar, having relative standard deviations below 2 % while the diesel fuel spiked sample concentrations have a much greater degree of variation with an RSD of 60 %.

#### Conclusions

With the increasing industrial use of polyelectrolyte based flocculation, the need to research and understand the fate of these products in the environment becomes a priority. Most anthropogenic substances introduced in the environment have direct and indirect toxic effects on the biota, sometimes even at relatively low concentrations. It is therefore essential to understand the behaviour of these substances in the environment, and their industrial use should be carefully monitored in order to early detect and manage an accidental discharge that could potentially harm the environment.

Determination of high molecular weight organic polymers in water is often difficult especially considering the fact that these substances, under environmental

|         | P1/P2 | P1/P3 | P1/P4 |
|---------|-------|-------|-------|
| CAL 1   | 0.84  | 9.14  | 5.07  |
| CAL 2   | 0.82  | 9.69  | 4.60  |
| CAL 3   | 0.82  | 9.72  | 4.60  |
| CAL 4   | 0.83  | 9.73  | 4.75  |
| CAL 5   | 0.82  | 9.76  | 4.67  |
| Average | 0.83  | 9.61  | 4.74  |
| SD      | 0.01  | 0.26  | 0.19  |

Table 1CALIBRATION SPECTRA PEAKRATIOS

|         | P1/P2 | P1/P3 | P1/P4 |
|---------|-------|-------|-------|
| BDW     | 0.83  | 9.84  | 4.70  |
| River 1 | 0.82  | 9.79  | 4.61  |
| River 2 | 0.83  | 9.78  | 4.65  |
| Diesel  | 0.35  | 12.76 | 1.43  |
|         |       |       |       |

Table 2A3040L AND DIESEL FUELSPIKED SAMPLES PEAK RATIOS

influence, can suffer alterations in their structure, generating a large number of different chemical species.

The use of chemical tracers for industrial reagents is a practice that is warranted only in few cases where the toxicity of the product requires exceptional attention and explains the significant additional costs that are necessary. Even in those cases where the use of tracers is required, their selection is difficult because they must have physical properties very similar to those of the marked toxic compound but also be easily detected and determined even in trace amounts.

This paper presents the development of an analysis method for the commercial A3040L product concentration in aqueous samples. The method is developed for the routine monitoring of effluents from the industrial units using this product. The developed method uses as analytical signal the FTIR absorption bands characteristic to a component of the product, namely the aliphatic hydrocarbon mixture used by the manufacturer to prepare the A3040L product.

Through the sample treatment steps and the FTIR signal evaluation, the developed method allows the removal of certain types of interferences and identifies the presence of other interfering substances. As such, the developed FTIR analysis method for the A3040L product can be used only for samples free of other major organic non-polar constituents, being especially suited in routine monitoring of the water treatment installations.

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