Gas-Chromatographic Technique for the Analysis of Flocculant PRAESTOL Content in Surface Waters

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The increasing amount of relatively new industrial reagents used is of concern especially when the full environmental fate of these chemical compounds is insufficiently documented. For some of these new reagents, the lack of analysis methods creates difficulties in the water quality monitoring of the discharged effluents. This paper covers the development and optimization of an analysis method for the Praestol A3040L content in water samples. Praestol A3040L is a moderately anionic polyelectrolyte containing acrylamide - sodium acrylate copolymers, ethoxylated alcohols and hydrotreated light petroleum distillates as an aqueous emulsion and it is industrially used in water treatment installations to promote the settling of suspended particles. Based on the reagent known constituents the method uses as analytical signal the GC-FID detection and quantification of its non-polar hydrocarbons, separated from the water sample by liquid-liquid extraction. The GC method optimization was primary focused at achieving adequate repeatability and detection limits and not for the individual chemical species separation, the method using the combined signal generated by the complex organic fraction. The best results were achieved with an injector temperature of 375 °C in split-splitless mode, a N_2, H_2 and air flow rate of 25 mL/min, 30 mL/min and 300 mL/min, a ratio of air:H_2 of 10:1, a carrier gas flow rate of 2 mL/min with an initial column temperature of 50 °C, followed by an increase with 20 °C /min up to 360 °C and a detector temperature of 360 °C. The method has a detection limit of 0.005 mg/L, a quantification limit of 0.01 mg/L with a repeatability of approximately 20 % and a linear calibration range up to 5 mg/L with a linearity coefficient of 0.997 (all concentrations being express as A3040L mass per aqueous sample volume).

Keywords: gas chromatography, PRAESTOL A3040 L, water treatment

In the context of meeting the legislation and sustainable development requirements, many research studies are aimed towards finding solutions for preventing, protecting against and mitigation of environmental pollution, finding new and better renewable energy sources and a better storage as well as , sorting and recycle procedures for hazardous, industrial, farming and domestic waste [1-6].

Already in some parts of the world, water scarcity promotes searching for cleaner industrial technologies with low environmental impacts. The need for cleaner industrial waste waters is brought by the increasing pressures on clean water sources needed to sustain a growing population [2-6].

Recently, the use of high molecular mass soluble compounds (flocculants) as reagents to accelerate the sedimentation or sludge dewatering processes for effluents containing organic and inorganic compounds from industrial, agriculture, medical and domestic sources is spreading [7, 8]. These reagents are used in addition to the biological stage to increase the water treatment efficiency [9, 10].

According to the Water Framework Directive (2000/60/EC) and European normative acts transposed at national level, before a new reagent may be used industrially it must be approved by the water regulatory institution, after laboratory studies are conducted to determine its safe environmental limits [11].

The polymers and surfactants are often associated in industrial applications due to their remarkable synergistic effects towards the aggregation of particles [12-14]. The complex formed by the surfactant - polymer mixture has better properties than the individual substances and thus preferred as interface for the dispersed or colloidal systems [4].

Praestol A3040L is an anionic polyelectrolyte with average molecular weight based on acrylamide – sodium acrylate copolymers (30 – 40 %) [9, 13, 14], ethoxylated alcohols (1 – 3 %) and hydrotreated light petroleum distillates (20 – 30 %) as a milky white aqueous emulsion. The optimal flocculant dosage is not only influenced by the copolymer properties (surface tension, viscosity and electrical conductivity), but also by the water composition [10, 14]. The flocculant toxicity and its insufficiently known environmental fate, enforce the necessity of effluent control and monitoring [15].

Praestol A3040L is usually used in conjunction with ferric chloride. The typical flocculant dose is 0.33 mg/L and the coagulant (ferric chloride) dose is 15 mg/L. The most important polyacrylamide reaction is the alkaline hydrolysis; the degree of hydrolysis may influence the flocculant efficiency and its viscosity [16]. It has been found that Praestol in combination with aluminum sulfate removes the water's color [9] as well as achieving effective treatment of natural water for consumption [17].

Considering its high affinity for fine suspended matter and colloidal particles, Praestol A3040L is used to remove suspended particles from aqueous media. The interaction mechanism between the polymer and the suspended particles is based on electrostatic affinity or hydrogen bond formation which leads to particle aggregation and the

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colloidal system destabilization. Because the particles become coarser, the solutions can be easily filtered and clarified [12, 19].

This paper covers the development and optimization of an analysis method for the Praestol A3040L content in water samples by gas chromatography. The method development start point was constituted by taking into account the various existing methods in the literature for the analysis of hydrocarbon content in different matrices [20-23]. Also, the sample pretreatment stages were optimized to yield more precise results and an improved analytical performance.

Experimental part

Materials and methods

The Praestol analytical signal was obtained using a gas chromatograph with a flame ionization detector and a direct injection/injection head-space autosampler.

Aqueous sample pretreatment steps include solvent extraction with hexane, organic extract purification on sodium sulfate and florisil packed columns, solvent removal by evaporation to dryness, residue dissolution in heptane and gas chromatographic analysis of the resulted aliquot.

Chemicals

The Praestol A3040L standard solution was purchased from Ashland (fig. 1) and the standard solution of n-alkanes in heptane was purchased from Fluka. The Florisil columns were purchased from Supelco and the solvents (hexane and heptane) with 99 % chromatographic purity were supplied by Scharlau. Magnesium sulphate and hydrochloric acid were purchased from Merck (Darmstadt Germany).

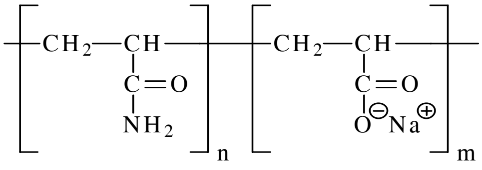

Fig. 1. The chemical structure of Praestol A3040L active ingredient (acrylamide - sodium acrylate copolymer)

Standard solution and calibration curves

The chromatograph operational parameters optimization was performed using an n-alkanes certified standard with a concentration of 50 mg/L [23]. The injected solutions were prepared with heptane and the chromatographic parameters were varied until optimal conditions regarding the analytical signal, repeatability and separation were achieved.

Results and discussions

The method sensitivity is influenced by operational parameters such as: the injector temperature, the hydrogen flow in the detector, the detector temperature, the column temperature.

Injector temperature optimization

The injector temperature optimization was carried out keeping all other chromatographic operational parameters constant and varying the injector temperature for consecutive 50 mg/L n-alkanes certified standard injections, monitoring the detector response (peak areas) (fig. 2). The injector temperature was varied between 330 and 380 °C in 10 °C steps.

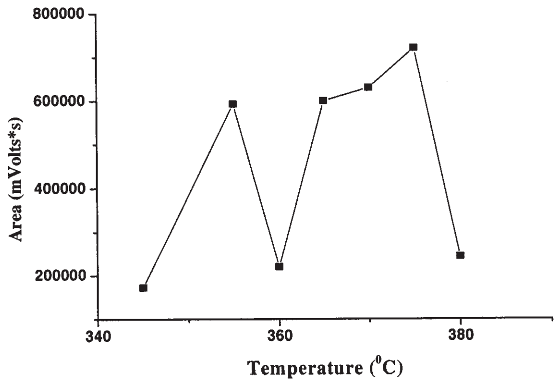

Fig. 2. The effect of injector temperature on peak area observed during the optimization

The best compromise between baseline shape, peak area and peak shape was obtained for an injector temperature of about 375 °C. At greater temperatures the thermo degradation of the analyzed compounds occurs.

Detector temperature and hydrogen flow optimization

The detector temperature and fuel (H_2) flow rate optimization was carried out keeping all other chromatographic operational parameters constant and varying first the detector temperature and second the H_2 flow rate for consecutive 50 mg/L n-alkanes certified standard injections, monitoring the detector response (peak areas) (fig. 3 and fig. 4). The detector temperature was varied between 300 °C and 370 °C. The detector fuel flow rate was varied between 10 and 45 mL H_2/min.

The best compromise between baseline shape, peak area and peak shape was obtained for a detector temperature of about 360 °C and a H_2 flow rate of about 30 mL/min.

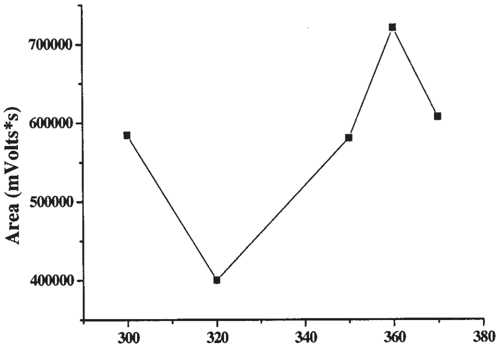

Fig. 3. The effect of detector temperature on peak area

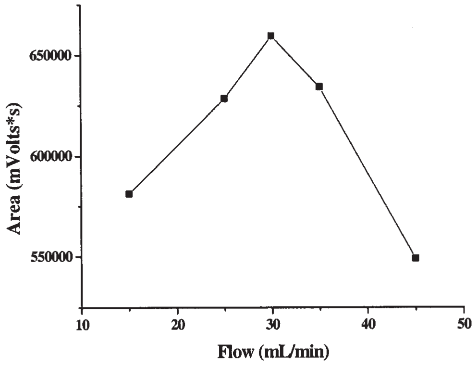

Fig. 4. The effect of the H_2 flow rate on peak area

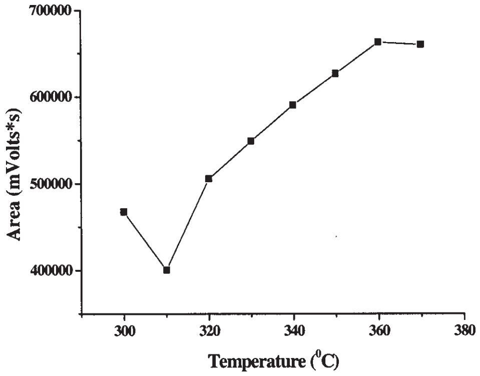

Fig. 5. The effect of column temperature on peak area

Column temperature optimization

The column temperature optimization was carried out keeping all other chromatographic operational parameters constant and varying the column temperature for consecutive 50 mg/L n-alkanes certified standard injections, monitoring the detector response (peak areas) (fig. 5). The column temperature was varied between 300 °C and 370 °C in 10°C steps.

The best compromise between baseline shape, peak area and peak shape was obtained for a column temperature of about 360 °C.

Extraction procedure

Due to A3040L high viscosity and glass adhesion phenomena, using pipettes or other volumetric means of dosing the required amount of product leads to significant negative errors caused by the impossibility of quantitative transference of the measured volume. All intermediary solutions were prepared weighting the required product mass directly in 100 mL class A volumetric flasks.

The water samples (900 mL), after the addition of magnesium sulfate (80 g), were acidified with 0.8 mL of concentrated hydrocloric acid and extracted with hexan (50 mL) for 30 min at 300 oscillations/min. The separated organic extracts were purified through anhydrous sodium sulfate – florisil packed glass columns and evaporated to dryness with a rotary evaporator. The organic residue was dissolved in about 6 mL of heptane and the obtained solutions were concentrated in a nitrogen stream up to a volume of 1 mL for GC analysis.

GC Analysis

The GC analysis was carried out using a Varian CP 3800 chromatograph equipped with flame ionization detector (FID) and CP 7491 capillary column (Select Mineral Oil).

Table 1

GC / FID OPERATIONAL PARAMETERS

Column	15 m x 0,32 mm ID x 0,10 μm DF
Injection	Split-splitless, split ratio 25:1, 375 °C, 1 μL injection volume
Carrier	Nitrogen: 25 mL/min, Hydrogen: 30 mL/min, Air: 300 mL/min
Oven program	50 °C to 360 °C at 20 °C/min (17 min analysis time)
Detection	FID 360 °C

The column carrier gas flow rate was set at 2 mL/min and the detector air:H_2 ratio was set to 10:1 (table 1).

Using the optimized operational parameters and the method pretreatment stages described above, solutions with concentrations of Praestol ranging from 2 to 4 mg/L (in respect to the aqueous phase) were analyzed (fig. 7).

The obtained chromatograms show that the analyzed organic phase is a mixture of various alkanes and iso-alkanes, with the individual components insufficiently separated. Nevertheless, the combined peak area for the timeframe between 4 and 8 min (fig. 6) may be used as analytical signal for quantitative determinations if the 3 peak clusters are recognized in the unknown sample chromatogram and no other major peaks are present in the respective timeframe.

Detection limit and quantification limit

For the evaluation of the method detection limit 10 blank samples were prepared and analyzed under repeatability conditions (fig. 8). The LOD derived from 3 times standard deviation of 10 blank samples is 0.005 mg/L and the quantification limit is 0.01 mg/L.

Repeatability

The repeatability of the method was determined analyzing 10 successive replicates of the n-alkanes certified standard (fig. 9) and 10 successive replicates of the Praestol solution (fig. 10). The relative standard deviation for the Praestol solutions was of about 20 %.

Linearity

The method linearity range was verified using 5 Praestol solutions with concentrations ranging between 1 and 5 mg/L in respect to the aqueous faze. The solutions were injected in the GC in ascending concentration order, obtaining the chromatograms depicted in figure 11. The obtained calibration curve has an acceptable linear

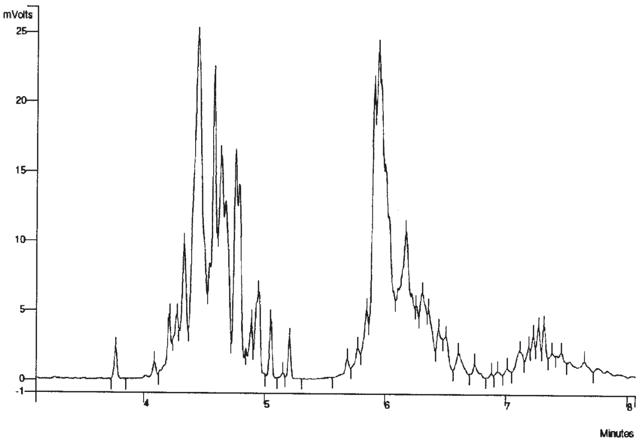

Fig. 6. Timeframe between 4 and 8 min. of the chromatogram depicting the Praestol analytical signal

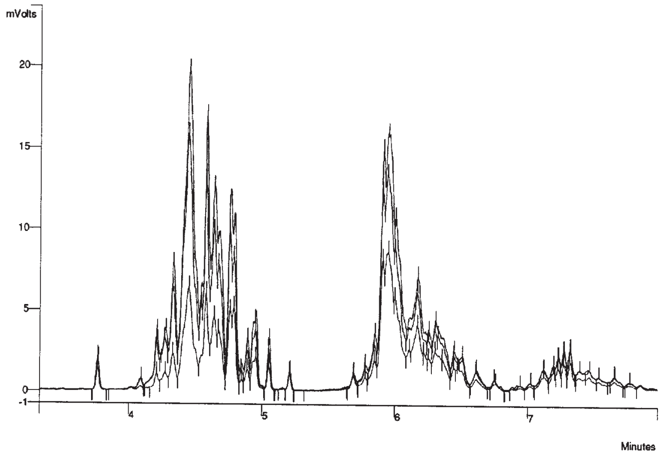

Fig. 7. Chromatograms for different concentrations of Praestol

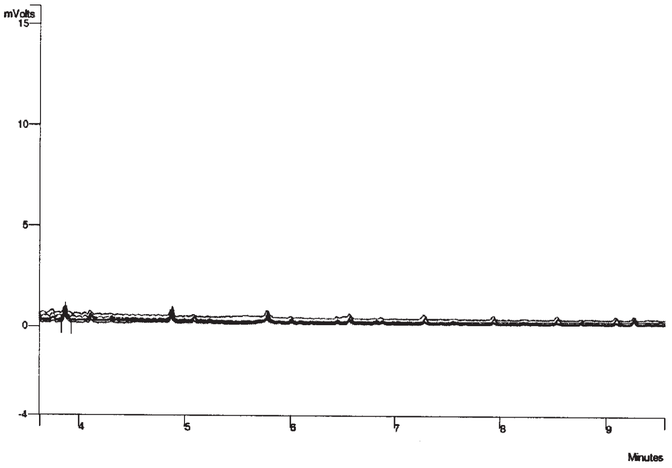

Fig. 8. Chromatograms obtained under repeatability conditions for 10 blank solutions

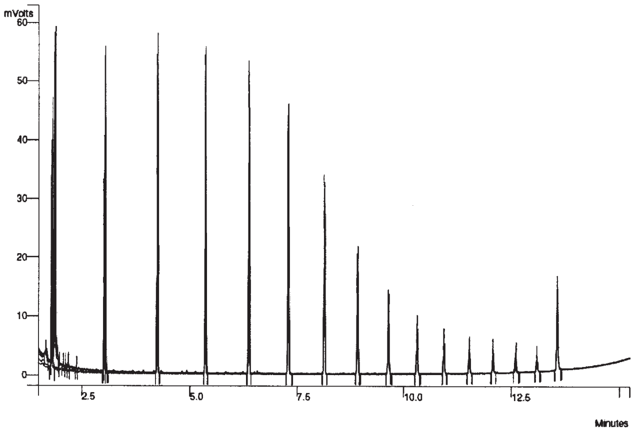

Fig. 9. Chromatograms of n-alkanes under repeatability conditions

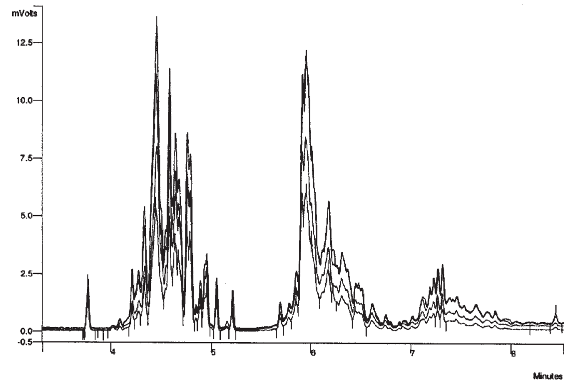

Fig. 10. Chromatograms of PRAESTOL A3040L under repeatability conditions

dependence between the combine peaks areas and the Praestol aqueous solutions concentrations with a correlation coefficient of 0.9975 (fig. 12).

Conclusions

The increasing amount of relatively new industrial reagents used is of concern especially when the full environmental fate of these chemical compounds is insufficiently documented. For some of these new reagents, the lack of analysis methods creates difficulties in the water quality monitoring of the discharged effluents.

This paper covers the development and optimization of a sensitive, selective and accurate analysis method for the Praestol A3040L content in water samples by GC-FID. The method uses as analytical signal one of the product constituents, namely its hydrotreated light petroleum distillates component.

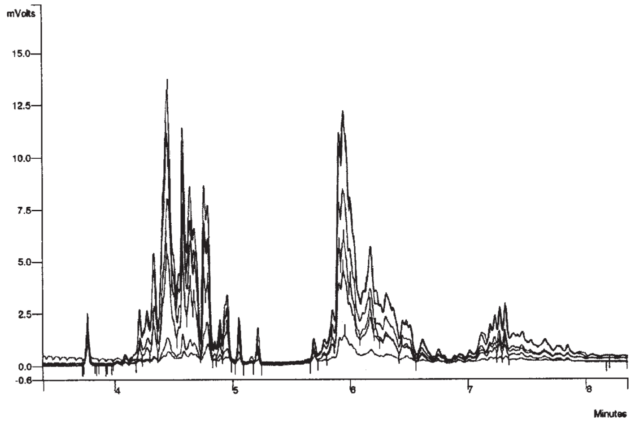

Fig. 11. Chromatograms for Praestol concentrations ranging from 1 to 5 mg/L

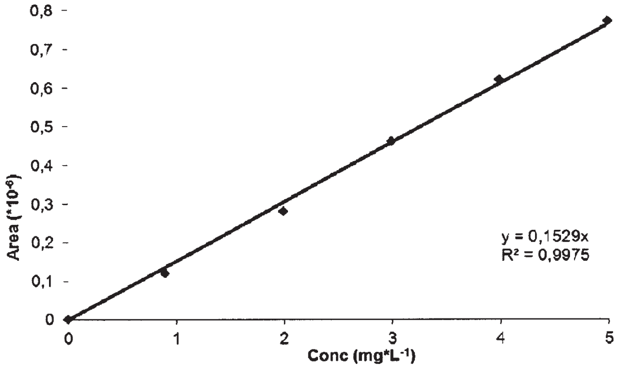

Fig. 12. Calibration curve for Praestol with concentrations ranging from 1 to 5 mg/L

The best results were achieved with an injector temperature of 375°C in split-splitless mode, a N_2, H_2 and air flow rate of 25 mL/min, 30 mL/min and 300 mL/min, a ratio of air:H_2 of 10:1, a carrier gas flow rate of 2 mL/min with an initial column temperature of 50°C, followed by an increase with 20°C /min up to 360°C and a detector temperature of 360 °C. The method has a detection limit of 0.005 mg/L, a quantification limit of 0.01 mg/L with a repeatability of approximately 20% and a linear calibration range up to 5 mg/L with a linearity coefficient of 0.997 (all concentrations being expressed as A3040L mass per aqueous sample volume).

The analytical performance criteria of the optimized method were suitable for the reagent detection and analysis from industrial effluents, the analysis method being included in a water quality monitoring program. The monitoring program results, evaluated in the context of the ecotoxicological data, allowed the safe industrial use of the Praestol A3040L reagent.

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Manuscript received: 8.04.2014