

The effect of surfactants upon spectrophotometric monitoring of the efficiency of removal of crude petroleum products from waste water by means of pressure-driven membrane processes

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Abstract: - In the presented research we have tested the application of photo ionization detector of ECOPROBE 5 analyzer to monitoring of low concentrations of petroleum products in water. Petroleum products are organic pollutants that are present in wastewater most frequently, which is caused by their broad applications and frequent incidents. Emergency leakage of petroleum and its products is predominantly caused by technical defects and operators' mistakes during transport, handling and storage of petroleum products. We tested the application of the mobile analyzer ECOPROBE 5 (RS Dynamics, Prague), which measures concentrations of organic substances in gas phase. It is sufficiently sensitive even for determination of milligram amounts of petroleum products in one liter of water. This principle of measurement can serve, e.g., as a basis of emergency alarm during long-term operation of membrane technology.

Key-words: - Crude petroleum products, waste water, pressure-driven membrane processes

1. Introduction

Crude petroleum products are the most often occurring organic pollutants, which is connected with their wide applications in various sectors suffering from frequent accidents. An emergency spilling of crude petroleum and its derivatives is mainly due to technological faults and mistakes on the side of operators during transport, handling and storage of these materials.

In technological practice the most frequently occurring materials are various sorts of petrol (mixtures of $C_4 - C_{12}$ hydrocarbons), kerosene (mixtures of $C_{12} - C_{18}$ hydrocarbons), gas oil (mixtures of $C_{16} - C_{24}$ hydrocarbons) and lubricating oil (mixtures of $C_{24} - C_{40}$ hydrocarbons). From the point of view of their composition, these materials contain both aliphatic and cyclic hydrocarbons, alkanes, alkenes and mono- and poly-cyclic aromatic hydrocarbons. In addition to hydrocarbons, also polar compounds are present, such as phenols, naphthenic acids, sulfur- and nitrogen-containing substances [1].

Crude petroleum products can be present in waters as dissolved or undissolved compounds, or can form emulsions, as the case may be. The water solubility of crude petroleum hydrocarbons varies within broad limits. For particular data, see Refs [2-

5]. From the literature given can be seen that the water solubility of these hydrocarbons decreases with increasing chain length.

The "solubility" of crude petroleum products in water is significantly affected by the presence of surfactants. According to literature data in Ref. [6], municipal waste water contains 10-20 mg of surfactants per liter. The presence of crude petroleum products in water significantly affects its taste and smell even at concentrations of 0.05 mg/l and higher [5]. Also the taste of fish meat is negatively affected, due to accumulation of these substances in fat tissue. Public notice No. 120/2011 restricts the content of crude petroleum products in drinking water by the value of 0.05 mg/l, the maximum allowed concentration in surface water being 0.2 mg/l [7].

The evaluation of properties of crude petroleum products in water is considerably complex, because they represent mixtures of compounds with various chemical structures and, hence, also various chemical, physical-chemical and biological properties. Therewith connected is also the problem of their analytical determination in waters.

In the Czech Republic, the crude petroleum products are estimated by means of parameter NEL

(Nepolární extrahovatelné látky = Non-polar extractable substances), which is defined in accordance with the standard Ref. [8] as a sum of concentrations of the substances which can be extracted by means of a hydrocarbon solvent having the boiling point in the range of 36-69 °C, substances which are not adsorbed on silica gel or Florisil, which can be determined by means of gas chromatography, and whose retention times lie between those of *n*-decane (C₁₀H₂₂) and *n*-tetracontane (C₄₀H₈₂).

Most frequently, the hydrocarbons are extracted with hexane. The extract is dried, and its polar components are removed by means of a polar sorbent, whereupon the content of hydrocarbons is determined by means of a gas chromatograph with flame ionization detector (FID). The result of analysis is a chromatogram, which provides the characteristic arc curve, the so-called fingerprint, which can serve the identification of individual crude petroleum products [9].

Moreover, the determination of crude petroleum products in waters can make use of the infrared spectroscopy. This test is based upon the extraction of non-polar substances from acidified water sample by means of suitable freon, the removal of polar substances by adsorption on silica gel, and subsequent measurement of IR spectrum in the wave number range of 2400-3400 cm⁻¹. From the ratio of absorption bands of the groups –CH₃, –CH₂– and =CH– it is possible to assess the proportions of aliphatic and aromatics hydrocarbons in the mixture [10].

Besides the analytical determination of crude petroleum products in laboratory, it is also frequently needed to arrange their continuous monitoring, e.g., for the purpose of determination of spreading of slicks on watercourses or checking of purification processes. For such purposes, various physical principles are used. For example, fluorescence detectors measure the fluorescence of aromatic hydrocarbons which is initiated by absorption of UV radiation from Sun [11]. A part of the Sun radiation absorbed by the film of crude petroleum products is reemitted into the atmosphere in the form of IR radiation, which can be detected by means of an IR camera.

The slick of crude petroleum products on the surface of oceans can also be monitored by means of radar [11]. The hydrocarbons on water surface can also be detected by an instrument using the impedance-capacitance principle [12]. The said literature references show that such sensors can be used rather for monitoring of higher concentrations of crude petroleum products, concentrations that

lead to formation of a continuous film on the water surface.

So far, there are several techniques for oil separation. Typical ones include chemical de-emulsification, pH adjustment, gravity settling, centrifugal settling, filter coalesce, heating treatment, electrostatic coalesce, membrane separation, etc. There are some advantages and disadvantages connected with each of these techniques.

Oil might be present in water as free (>150 μm), dispersed (150-50 μm), emulsified (50-0.1 μm), and/or soluble (<0.1 μm) form. Free and dispersed forms are efficiently removed by gravity in oil/water separator devices. Emulsified fraction consists of stable oil droplets, which have to be destabilized before removal [13].

One of the advantages of ultrafiltration (UF) compared with the other separation processes is the capability of removing emulsified oil droplets without any de-emulsification processes. Ultrafiltration has been demonstrated as an efficient method or a pretreatment step before nanofiltration (NF) and reverse osmosis in oil/water emulsions treatment [14-16].

With regard to the fact that the pressure-driven membrane processes are predominantly used for final purification of water, it is necessary to have at one's disposal a monitoring device that allows monitoring of water concentrations of crude petroleum products at the level of the order of magnitude from 10⁰ to 10⁻¹ mg/l.

2. Theoretical

The crude petroleum products partially dissolve in water, but mostly they form emulsions or –at higher concentrations – they produce a film on the water surface.

An emulsion is a mixture of two immiscible or partially miscible liquids. The stability of such emulsion can be described as inclination to reverse separation of these two liquids. Such separation is called emulsion breaking (complete demulsification). In the simplest case, this inclination can be described by means of the Stokes law (1), which is most often used for sedimentation. In the case of oil-in-water emulsion, the process is not sedimentation but an opposite process – creaming: the size of oil droplets is not changed and these droplets separate from the mixture by rising up to the surface. Other processes, such as aggregation of droplets, coalescence, the Ostwald ageing, can be considered to be accompanying phenomena that

accelerate the creaming. The said equation shows that the emulsion stability is particularly affected by the droplet size of dispersed substance, i.e. oil droplets in our case of oil-in-water emulsion. Another factor is the viscosity of medium (i.e. water) and, of course, the density difference between dispersed substance and medium

$$u_{oil} = \frac{2(\rho_{water} - \rho_{oil})r_{oil}^2 g}{9\eta_{water}} \quad (1)$$

Surfactants are surface-active substances which can decrease the surface tension and thus enable formation of smaller, stable oil droplets. With respect to the specific structure of surfactants, these compounds—even at very low concentrations—change the reaction conditions at the phase interface. By specific interactions with the molecules of dispersion medium they markedly affect the energy conditions at the interface, which results in lowering of surface tension. This fact is due to asymmetric bipolar character of surfactant molecules, with distinct dipole moment. They contain a hydrophobic and a hydrophilic part. The former repulses water but can interact with non-polar ingredients in water. The hydrophilic portion of surfactant molecule has a high affinity to water and ensures mutual mixing of the non-polar substances in water, which can be described as solubilization.

By their behavior in aqueous medium, surfactants can be divided into two classes: ionic ones, which in aqueous solution dissociate to give surface active ions, and non-ionic ones, which contain a large amount of non-dissociated polar groups, e.g., $-\text{OH}$ or $=\text{O}$.

About 60 % of all surfactants manufactured belong to the group of anionic ones. These include soaps, alkyl sulfates, alkylsulfonates, alkylbenzenesulfonates and sulfated non-ionic surfactants. Apart from soaps, which are easily biodegradable, anionic surfactants remain in waters relatively long and cause foaming.

From among the cationic surfactants the most frequently used are quaternary ammonium and pyridinium compounds containing at least one long hydrophobic chain. The cationic surfactants are used because of their disinfectant effects. In waters they have toxic effects upon aquatic organism and are decomposed only slowly. Anionic and cationic surfactants can react with each other and produce little soluble compounds.

The class of ionic surfactants also includes ampholytic surfactants, which contain in their molecules both acidic and basic hydrophilic groups. Depending on pH, they can behave as either anionic substances or cationic substances [1].

The most widespread non-ionic surfactants are adducts of ethylene oxide. The hydrophilic part of their molecules is formed by a poly(ethylene oxide) chain. The hydrophobic part is a long hydrocarbon chain which is attached by means of ester, amide or ether bond. Easily biodegradable representatives only include the compounds with straight-chain alkyl group and a small number of added ethylene oxide molecules.

As a rule, surfactants are applied in the form of detergents. They are preparations used for washing and cleaning. Besides the surfactants, they contain other activation additives and filling agents, and, as the case may be, also optical brighteners, dyestuffs, perfumes etc. [1]

Due to widespread applications of surface active preparations, which serve as washing agents, emulsifiers, dispersants, wetting agents and foaming agents, the waste waters are considerably contaminated with them.

In literature [17] we can find the temperature dependence of dissolution of all existing binary systems present in ternary-system water-oil-surfactant (see Fig. 1). Here it is seen that there exist a certain limitation on miscibility between surfactant and oil. After exceeding the upper critical temperature of miscibility, T_{α} , a homogeneous solution is formed. In the binary mixture water-surfactant we can see a bounded area. The closed loop is due to the breaking of hydrogen bonds upon heating and shows up for strong amphiphile surfactants. Thus for dissolution of surfactant in water there exist two upper critical temperatures and one lower critical temperature, T_{β} .

The ternary diagram proper (Fig. 2) can be found in literature (Refs. [6, 18]). In its simplest form, this diagram is divided into two parts. Under the curve there is a two-phase area. Above this binodal curve there is the area of micro-emulsion (micellar phase, m-phase). For naked eye, this area appears as a homogeneous solution; yet in fact it is always an emulsion. What is small for a naked eye is not small for neutrons. Therefore, this phenomenon (called solubilization) must not be confused with dissolution.

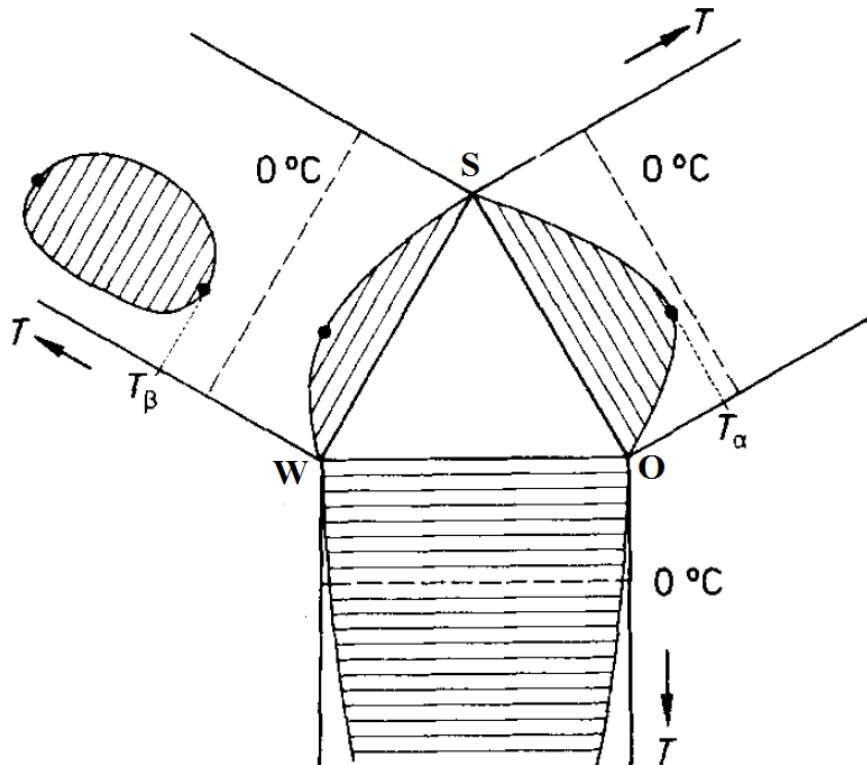


Fig. 1.: Temperature effect on solubility for binary systems

Also such situation may arise when we find ourselves in the area of insolubility of the surfactant; a three-phase area is then formed. This situation is represented in Fig. 3, TYPE III. The authors of paper Ref. [18] generally give a true picture of the effects of individual parameters upon the transition between the types I-II-III.

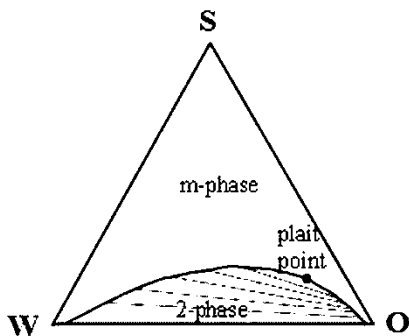


Fig. 2.: Generally ternary diagram for system Water-Oil-Surfactant (W-O-S)

For instance, for increasing temperature the valid transition is I-III-II. This is explained by the fact that especially non-ionic surfactants at lower temperatures have a higher affinity for aqueous phase, whereas at higher temperatures for oil. This will make itself felt by reversal of direction of tie lines in the heterogeneous part of the diagram. If the

surfactant exhibits the above-mentioned “insolubility” under the given conditions, there exists area III between this transition.

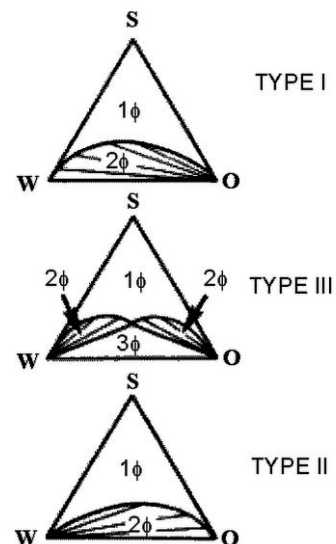


Fig. 3.: The Winsor diagrams for ternary system W-O-S

However, a certain amount of surfactant is able to solubilize only a certain amount of oil. This amount is called the maximum additive concentration (MAC). There exist many factors

which affect the solubilization. The main of them are as follows: the type (kind, structure) of solubilizer (surfactant), the solubilized substance (oil), temperature, ionic strength of the solution, additional substances (co-surfactant).

It is obvious that if a particular analytical method is based on monitoring of concentration of the substance in vapors, then this concentration will be higher in the case of samples having a higher concentration of oil on the surface. In this case, evaporation particularly concerns the lower hydrocarbon fractions in light heating oils (in Czech: lehké topné oleje = LTO). The surfactants that are generally present in waste water will solubilize the oil and thereby lower the oil concentration near the surface and hence in vapors.

3. Experimental

The purification of waste waters containing crude petroleum products was performed using the apparatus depicted in Figs 4 and 5. The circulating loop was constructed from stainless steel and contained a ten-liter feed suspension reservoir (2), pump (3) and the membrane module (5). This loop was also equipped with a pressure (4) and flow (7) monitoring system. The cross flow velocity was

controlled using the speed of the pump and the operating pressure (and hence trans-membrane pressure) in the loop was controlled by a needle valve (6) at the module outlet; both parameters were varied independently. The loop was also equipped with a temperature regulating system (1). The permeate flux was measured by the balance (9) connected with PC (10).

Fig. 5 presents the real version of the apparatus (Minipilote – ORELIS Environnement).

Firstly, the purification process was tested using the model samples prepared by mixing of defined amount of LTO with pure drinking water; secondly, waste water obtained from car wash was purified. The initial concentration of LTO in waste water varied in the range of 2-15 mg/l.

If the membrane technology is continuous, it will be necessary to equip the technological apparatus with a sensitive detector, which will monitor the progress of purification process. For this purpose, we tested the application of mobile analyzer ECOPROBE 5 (RS Dynamics, Prague), which measures the concentrations of organic substances in gaseous phase. The instrument is represented in Fig. 6. It is equipped with two detectors: infrared (IR) and photo-ionization (PID).

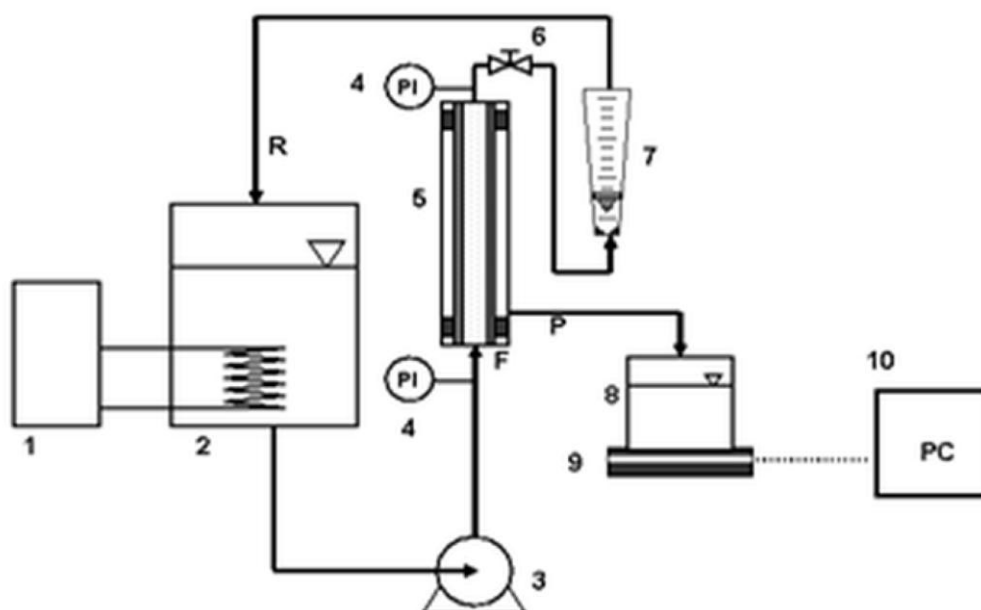


Fig. 4.: Scheme of experimental apparatus for microfiltration/ultrafiltration (MF/UF) experiments



Fig. 5.: Real picture of experimental apparatus for MF/UF experiments

For the purpose of monitoring of crude petroleum products in water it is necessary to use the photo ionization detector (PID), which does not detect water vapors. It operates on the principle of ionization of the substances in measuring cell by means of irradiation provided by a UV lamp. A scheme of the analyzer is given in Fig. 7. The analyzed gas passes through the measuring cell where it is exposed to irradiation from UV lamp.

The radiation ionizes the gas to give positively and negatively charged ions. These charged particles enter the space between two electrodes carrying a definite voltage. The presence of charged particles will make itself felt by currents of various intensities; after amplification, their magnitude is displayed on the monitor of the apparatus. After the ionized gas has passed through the cell, the ions undergo recombination and the gas comes out from the apparatus in original state.



Fig. 6.: Measuring instrument ECOPROBE 5 – an example of calibration

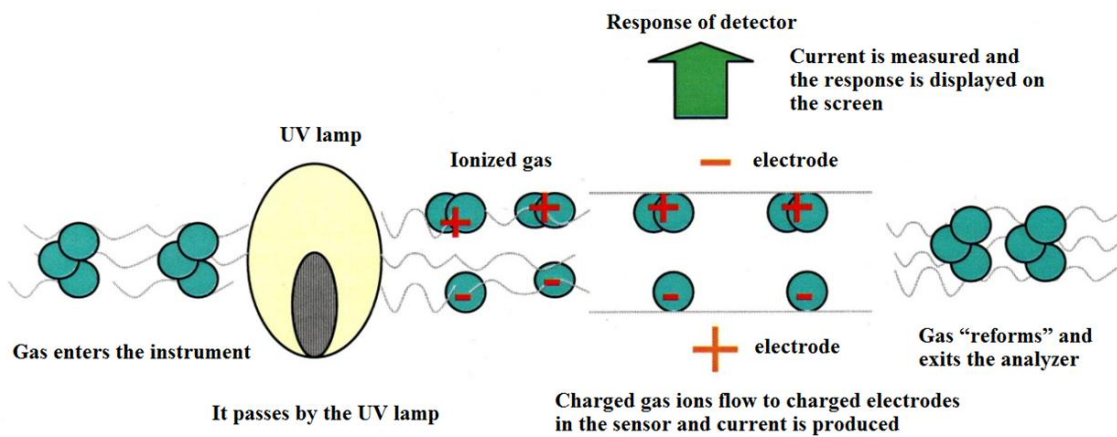


Fig. 7.: Scheme of PID analyzer

The PID analyzer can operate in two working modes. The first of them is HI-SENS (highly sensitive regime); it enables measuring of substances in gas at the maximum concentration of 100 ppm. The results are presented in ppb or $\mu\text{g}/\text{m}^3$. The second is the mode STANDARD, for which the manufacturer states that it can measure up to the maximum concentration of 4000 ppm with the detection limit of 0.1 ppm.

The application of the analyzer to the monitoring of very low concentrations of crude petroleum products in water was tested using the apparatus depicted in Fig. 8.

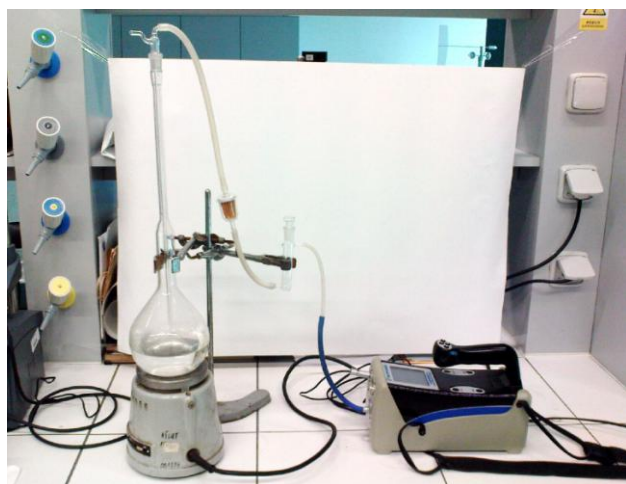


Fig. 8.: Test apparatus

It consists of a long-neck glass flask, magnetic stirrer, absorber with potassium hydroxide, and measuring apparatus ECOPROBE 5.

The glass flask was used as a container of contaminated water. This water was intensively stirred with the magnetic stirrer, which resulted in higher distribution of volatile components of crude petroleum into gas phase. The gas to be measured has to be rid of water vapor, which otherwise would condense in the measuring cell of photo-ionization detector and affect the resulting values of measurement. This was achieved by passing the collected gaseous sample through a layer of potassium hydroxide. The suction of sample and the measurement proper were performed by means of the test analyzer ECOPROBE 5.

4. Results and Discussion

The monitoring of content of crude petroleum products in water by means of photo-ionization detector of analyzer ECOPROBE 5 is based on the analysis of vapors above the aqueous

solution, where there are volatile hydrocarbons at concentrations that are proportional to their content in the aqueous phase. During the measurement, it is necessary to maintain constant temperature and constant stirring speed of the water sample. The results of measurements of hydrocarbon concentrations above the solution with defined content of LTO are given in Figs 9 and 10. Since the sample was introduced into the glass flask in batches, the repeated measurement of the vapors above the solution was connected with stepwise removal of volatile substances. The gaseous samples were collected by suction at the distance of 1 cm above the surface of stirred sample. Each of the obtained curves exhibit a maximum; if the values of these maximum responses of the analyzer are plotted against the LTO concentrations in the solutions (Fig. 10), then a linear dependence is obtained, which proves that the LTO concentration in the solution can be evaluated on the basis of the PID response. The picture also shows that the photo-ionization detector operating in the HI-SENS mode is sufficiently sensitive even for monitoring (in the order of magnitude) of 10^0 mg/l concentrations of crude petroleum products in water.

Since surfactants are always present in sewage waste waters, attention was subsequently focused on the effect of their presence on the volatility of volatile components present in crude petroleum products, which can significantly influence the process of monitoring of water contamination.

Model aqueous samples were prepared with the LTO content in the concentration range of 1-10 mg/l in the presence of different amounts of detergent – Jar-Lemon (which according to the manufacturer's statement contains 5-15 % of anionic surfactant and less than 5 % of non-ionic surface active agent). The concentrations of this detergent varied in the range from 0.025 g/l to 0.1 g/l in the model solution.

The prepared model solutions in a calibrated flask were intensively stirred 5 min, whereupon followed the analysis of vapors above the solution, the measurement conditions being adjusted to 5 sec pre-integration period and 30 sec the recording proper of the measured values. Throughout the integration period, the measured concentrations exhibited a constant value, which proves the fact that in the course of monitoring the gaseous atmosphere above the solution was not significantly diluted. The temperature of solutions varied in the range of 23-23.5 °C. The obtained results are presented in Figs 11 and 12.

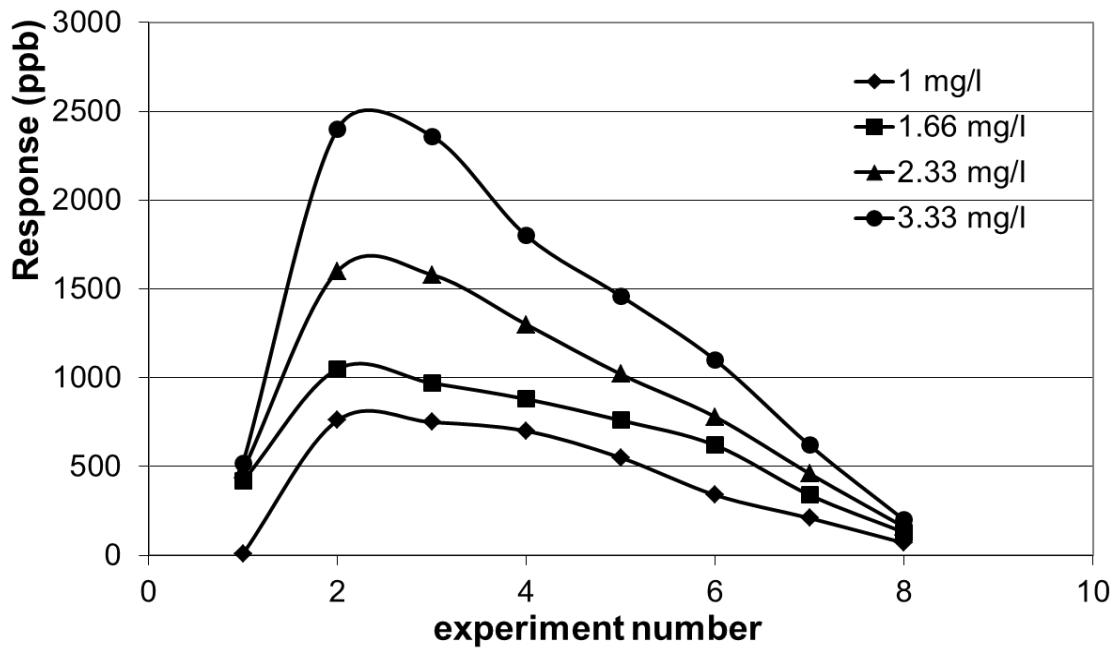


Fig. 9.: Response of ECOPROBE 5 in a series of 8 measurements

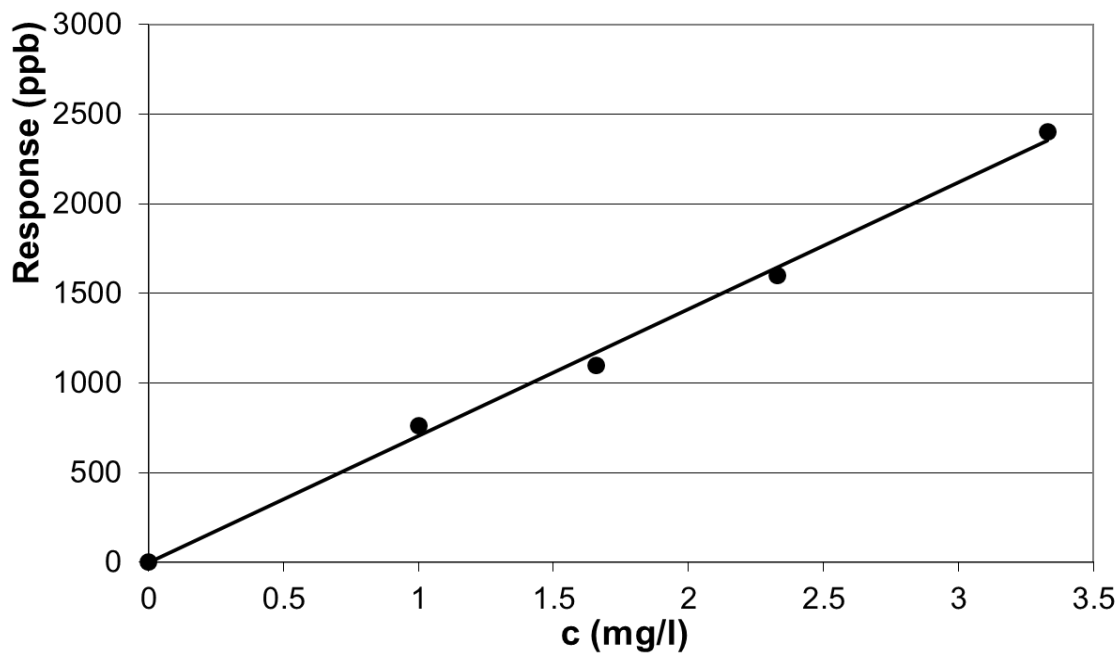


Fig. 10.: Dependence of response maximum on LTO concentration

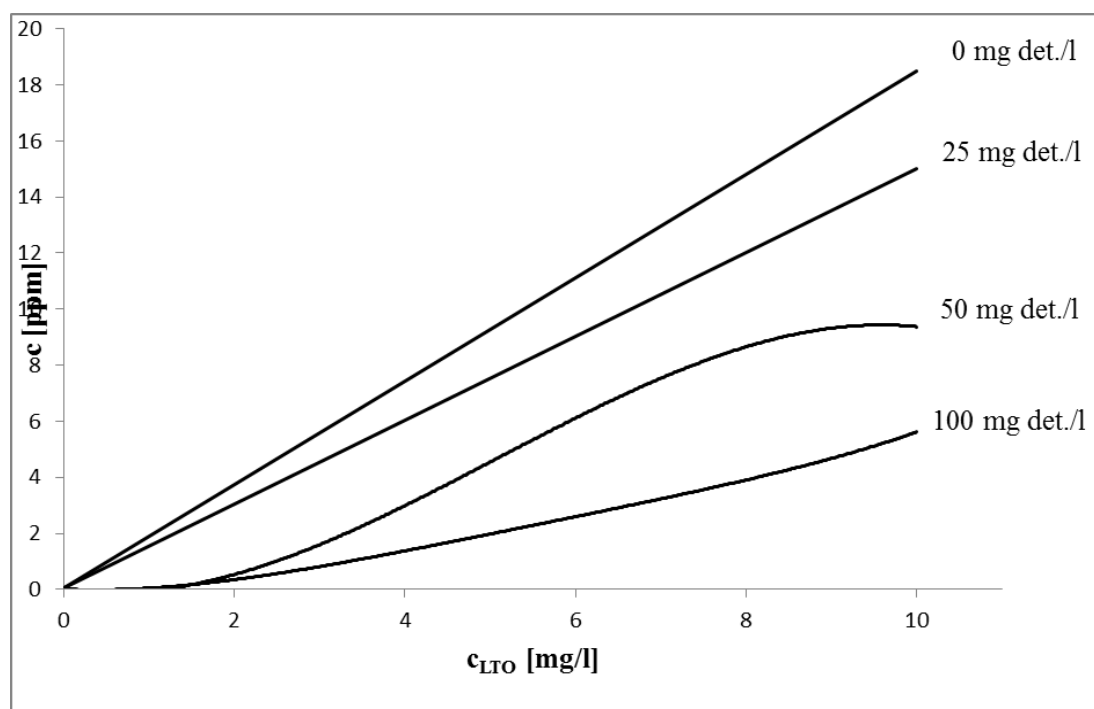


Fig. 11.: Effect of amount of surface active agent on vapor concentration above LTO solution

From Fig. 11 it is obvious that the presence of surfactant lowers the concentration of volatile crude petroleum components above the solution. For instance, at the LTO concentration of 10 mg/l, the value from ECOPROBE 5 decreases by about 50 % in the presence of 50 mg/l surfactant, as

compared with the vapor concentration above the same LTO solution without surfactant; if the surfactant concentration in the mixture is 100 mg/l, then the vapor concentration above the solution reaches ca 28 % of the original signal above the water contaminated only with LTO.

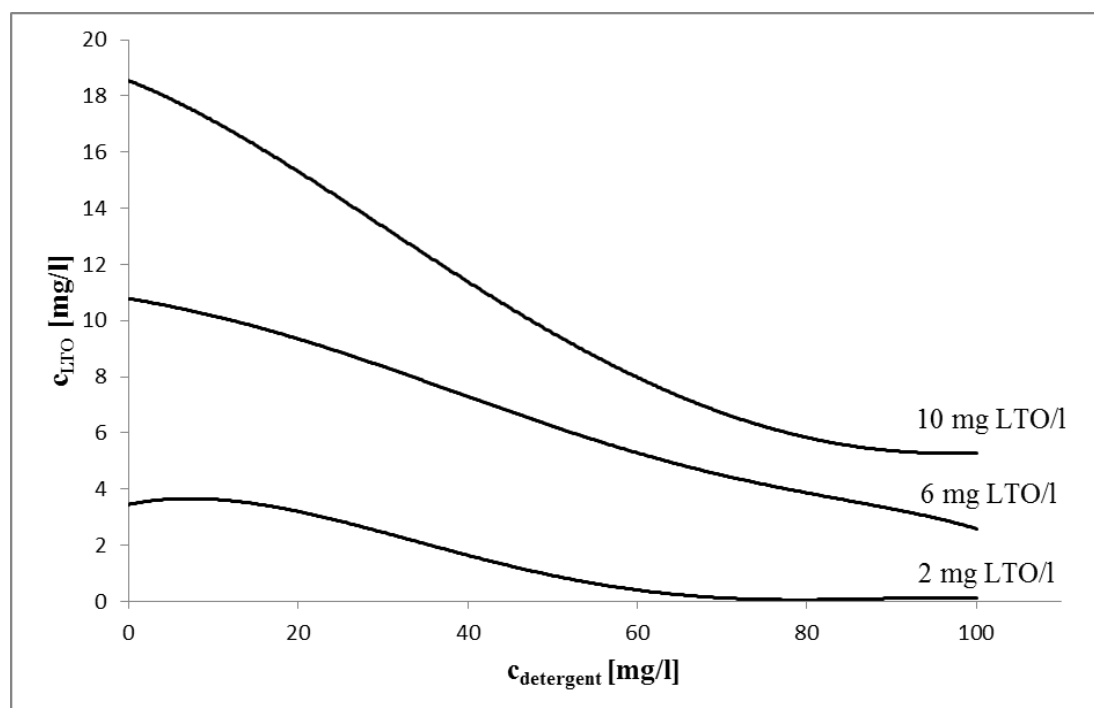


Fig. 12.: Effect of volatility of volatile substances present in LTO depending on the amount of surfactants in solution

The influence upon volatility of selected LTO concentrations in the presence of different amounts of applied detergent Jar-Lemon is given in Fig. 12. The diagram shows that the concentration of volatile substance above the solution decreases significantly (but not linearly) with increasing concentration of the surface active agent in the solution.

On the basis of the fact found it can be stated that the presence of surfactant significantly affects the solubility of non-polar crude petroleum substances in water and, subsequently, also the distribution of volatile substance into the gas phase above the solution. Due to that, the sensitivity of the chosen method is decreased, and it is necessary to perform the monitoring in the HI-SENS regime.

The application of this measuring principle in practice is expected primarily to the checking of operation of membrane technology.

All tested UF membranes (US100, UP020 and US005) show more than 92% oil rejection within the feed concentration range for binary system LTO-Water. For real waste water was used only MF membrane MV020, and this membrane reached the maximum oil rejection of 72.2 %. We presume that this type of membrane will be used as pretreatment before UF stage, because this membrane retains suspended solids and this improves performance and the flux of permeate during ultrafiltration.

5. Conclusion

The paper describes tests of applications of photo-ionization detector of mobile analyzer ECOPROBE 5 to monitoring of low concentrations of crude petroleum components in waste water.

It was found that, after perfect removal of water vapor, the analyzer provides a linear response to increasing LTO concentration in the solution. It is sufficiently sensitive for determination of crude petroleum components at concentrations of the order of magnitude of 10^0 mg/l. This measuring principle can serve, e.g., in the case of announcing an emergency situation in long-term operation of membrane technology.

Acknowledgements

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