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On-line express-analyzer and method of water monitoring on the base of proton magnetic resonance

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Annotation. Described flow analyzer of water on the presence of impurities, based on proton magnetic resonance - PMRA. Presented common appearance and construction, mode of operation PMR-analyzer. Presented equations of received dependences for determination of salts and oil impurities in water. Proposed structure and technologic schemes for removal of impurities from water in the installation with rotating magnetic and nonuniform electric field with continual on- line control of water purity bu flow PMR-analyzer.

Introduction

Last years observed increasing mining of high water containing (up to 98%) oils in the form of high disperse emulsions, separation of which is a sufficient problem. It is connected with their high stability due to great asphaltenes concentration. After separation of such emulsions water inevitably contain impurities in the form of oil droplets and diamagnetic/paramagnetic salts of oil stratum waters. In all the case it is poured in surface waters, which are used for heat stations and localities water supply.

The quality of drainage water is regulated and must satisfy resolution of International committee on the protection of sea waters MEPC.107(49) by 18.07.2003 (not more, than 15 mg/l of oil).

At present time concentration of oil in water can be measured by laboratory analyzer KN-1 (Ecros) in the range of 0,05-50 mg/l as well as of 0-1000 mg/l by dissolving of the sample in CCl₄. In flow mode it can be controlled by signalyzer Fluorat AE2 (analyzer is not present), which signalize the oil presence in water in the range of 0,01-10 mg/l with accuracy $\square$ 10%. In the measurement process is used extract of oil from water byheksane (10 mg of heksane on 100 ml of sample). Measurement time is 15-30 minutes.

Among foreign analyzers must be mentioned OCMA-300 HORIBA (Bella-Diffusion, France) and ELE International with measurement range of 0,01-200 mg/l (ppm) and accuracy $\square$ 10%, based on the near infrared (NIR)-spectroscopy. For sample preparation is used dissolver Horiba S-316. Measurement time – 15-30 minute.

Flow (on-line) PMR express – analyzer for water quality monitoring

For monitoring of water quality, used in the heat stations and for industrial purposes we proposed elaborated and having no analogues flow express-analyzer on the base of proton magnetic resonance - PMRA. On the fig. 1, 2 presented common view and functional scheme of the first generation PMRA-I [1].



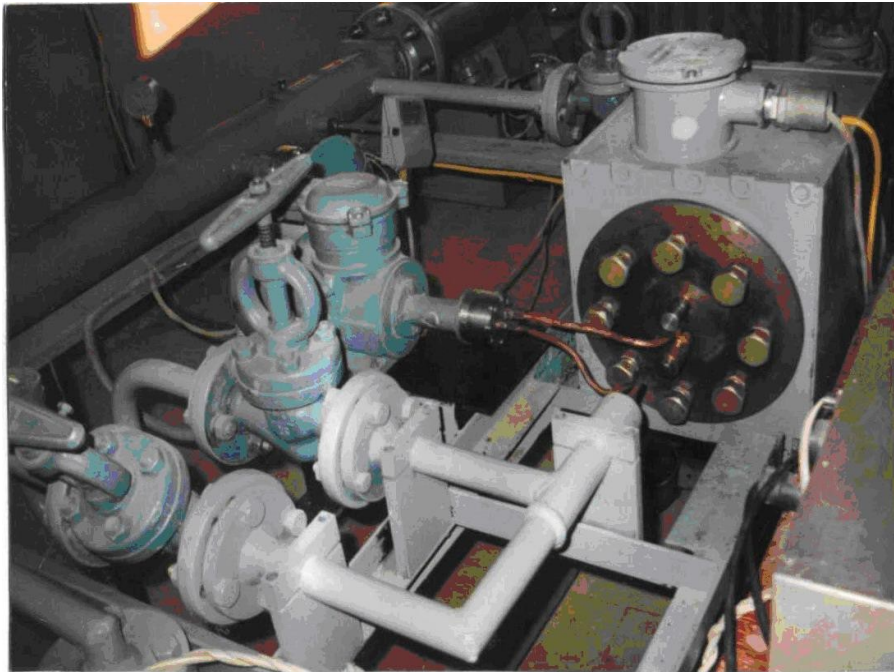


Fig.1. Flow (on-line) PMR-analyzer

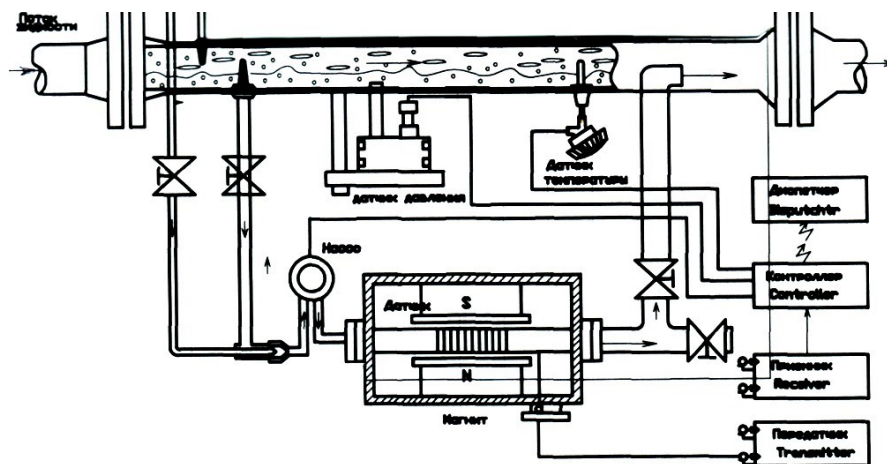


Fig.2. Functional scheme of flow (on-line) PMR-analyzer

Express mode of analysis is the foundation of the PMR method, which is attributed to methods with inner standard, noncontact and not destroying, does not need sample preparation. Time of measurement depend from number of accumulations n , increasing measurement precision in $\sqrt{n}$ times and in mean time of measurement equals 2-3 minute.

Controlled media – water-oil and gas mixtures; temperature of measured mixture is $+5 - +50^{\circ}\text{C}$, temperature of environment $-60^{\circ}\text{C} - +50^{\circ}\text{C}$, pressure 0.1 - 6.4 MPa, permissible pressure drop on the analyzer is 0,25 – 0,5 MPa, density of the media 400 - 1100 kg/m^3 . Working mode is automatic, continuous-cyclic. Length of the communication line of analyzer with controller of computer - $\lambda/4$ (near to 15 m on the resonance frequency 3 MHz). Measurement results through radiochannel is translated on the central control panel of measurement installations.

Method of salts and oil in water determination by the data of pulse nuclear (proton) magnetic resonance method [2]. Concentration of diamagnetic salts in water

For determination of NaCl, CaCl₂, MgCl₂ salts C_B (mol/1000 g H₂O) concentration in water, may be used dependences of proton relaxation rates $(T_{1B})^{-1}$ from salts concentration.

Especially, for NaCl dependence for C_B of salt in water from relaxation rate $(T_{1B})^{-1}_{NaCl}$ (in solutions $T_{1B} \equiv T_{2B}$), can be approximated with regression coefficient $R^2 = 0,9962$ by equation:

$$C_B = -42,765 + 220,9 (T_{1B})^{-1} + 247,8 (T_{1B})^{-2} \quad (1)$$

For CaCl₂ – with regression coefficient $R^2 = 0,9996$ by equation:

$$C_B = -4,55 + 20 (T_{1B})^{-1} + 9,7 (T_{1B})^{-2} \quad (2)$$

For MgCl₂ – with regression coefficient $R^2 = 0,9924$ by equation:

$$C_B = -2,23 + 9,8 (T_{1B})^{-1} + 3,99 (T_{1B})^{-2} \quad (3)$$

Every diamagnetic ion, contained in solution, has its own coefficient of relaxation effectiveness. In stratum water, remained after its separation from oil-water emulsion, dominantly presented salts of NaCl, CaCl₂ and MgCl₂ in the proportion 73:20:7. That's why for mixtures of this salts we must use equation, considering contribution of all of them:

$$C_B = k_{C1} + k_{C2} \{P_1 (T_{1B})^{-1}_{NaCl} + P_2 (T_{1B})^{-1}_{CaCl_2} + P_3 (T_{1B})^{-1}_{MgCl_2}\} = \\ = -32,284 + 165,94 (T_{1B})^{-1} + 183,1 (T_{1B})^{-2} \quad (4)$$

Here for stratum water $P_1 = 0,73$, $P_2 = 0,2$, $P_3 = 0,07$.

Concentration of oil in water

Determined by us dependences between PMR relaxation parameters and summarized signal amplitude $A_{\Sigma 1}(C_{H1})$ for the range 0-300 mg/l and $A_{\Sigma 2}(C_{H2})$ for the range 0-30 000 mg/l are described with regression coefficients $R_1^2 = 0,9976$ и $R_2^2 = 0,9812$ by equations:

$$C_H (\text{мг/дм}^3) = -58,42 - 0,23 A_{\Sigma 1} + 0,006 A_{\Sigma 1}^2 \quad (5)$$

$$C_{H2} (\text{г/дм}^3) = -102,4 + 0,877 A_{\Sigma 2}, \quad (6)$$

Concentration of paramagnetic salts in water

Determination of soiling of pollution waters by heavy (paramagnetic) metals salts (integral index) and elemental composition by using method of addition or complex-formation is performed in the range from

0.05 mg/l up to saturated solution with relative precision $\pm 4\%$ by equation:

$$N = K_{1(2)-1} [(T_{1(2)-1})_{изм} - (T_{1(2)-1})_0] \quad (7)$$

where $(T_{1(2)-1})_{изм}$ and $(T_{1(2)-1})_0$ - relaxation rates, measured in the sample of polluted water and in distilled water without paramagnetic ions, $K_{1(2)}$ – coefficient of relaxation effectiveness.

Minimal measured paramagnetic ions concentration N_{min} is determined by the difference between $(T_{1(2)-1})_{изм}$ and $(T_{1(2)-1})_0$, i.e. by apparatus precision, which can be characterized by coefficient f . Then :

$$N_{\min} = (T_{1(2)})^{-10} (f-1)/K_{1(2)} \quad (8)$$

Increasing of the measurements precision decrease lower limit of measured concentrations.

For the paramagnetic ions mixture with different concentrations can be used method of addition. Initially is prepared solution with known ion concentration N_2 and in doses it is added in measured sample with N_1 ion concentration. Then is measured relaxation rate $(T_1(2)-1)_{изм}$ and is drawn up graph of $(T_1(2)-1)_{изм} / N_1$ dependence from N_1-1 . Tangent of slope angle of this line is equal to N_1/N_2 .

Cleaning of water from impurities (ions and oil droplets) in the rotating magnetic and nonuniform electric fields with permanent on-line control of water quality by flow PMR express-analyzer [3].

For purifying of water in the form of fine disperse distributed oil emulsion and diamagnetic/paramagnetic salts the use of standard industrial installations, based on thermal affect is embarrassing due to their resource- and energy consumption. Industry need compact installations with low energy consumption and which use methods of soft affect by physical fields, which does not cause additional droplets dispergation and does not need reagents to use. For this aim we propose installation [3], presented at fig.3.

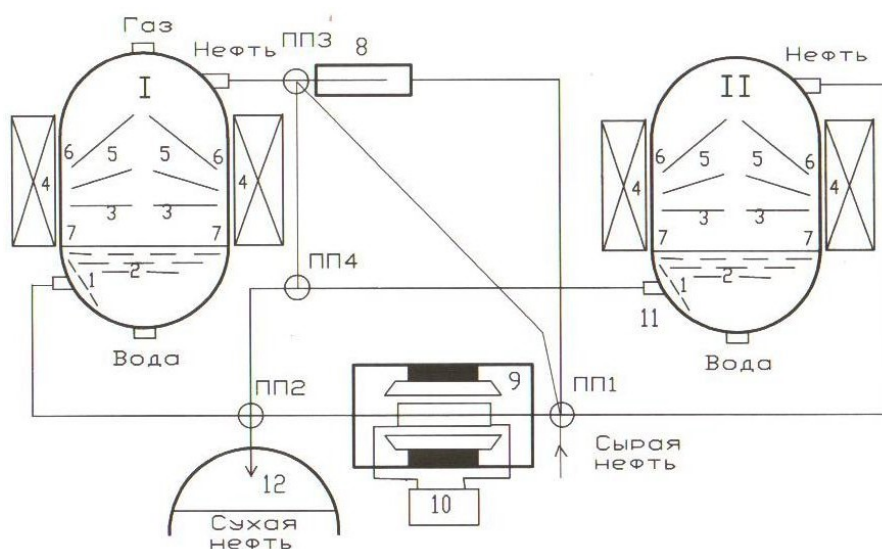


Fig.3. Block for emulsions destruction in the rotating magnetic and nonuniform electric field and installation for process control by flow PMR-analyzer.

Method of water purifying from impurities include the following stages:

1. Water emulsion through three way flow switcher III1 feed to the input control in PMR-analyzer 9 for the determination of emulsion parameters to choose process mode – electric fields tension, magnetic field induction, flow velocity, charge on the net 1 of block I for water separation from oil. Then through flow switcher III2 emulsion is feed in block I and flow through charged net 1, where droplets and impurities get charges determined by equation:

$$q \approx 1,64 E_0 r_0^2 \quad (9)$$

Charged impurity (oil droplet, salt ion) is pushed from the net 1 with the force:

$$F \approx 1,37 E_o^2 r_o^2 \epsilon_{cp} = 0,835 q E_o. \quad (10)$$

The flow feed can be performed not on radius direction but by perimeter side of trunk in the direction coinciding with the electrodes rotation. This leads to the turning of emulsion flow and additional centrifugal force, throwing impurities off to the outer perimeter of block I.

2. Beyond of precipitated water layer is settled intermediate layer with petty droplets, where they coalescence, subjected by treatment of electromagnetic (EM) fields, rotating magnetic field, created by windings 4 and simultaneously nonuniform DC and AC electric field, formed between water surface and several electrodes 5 with AC/DC tension, while field quantity between electrodes 5 is changed (increased) with the electrode higher position on the rotor in block I. Such demand of specific electric field E_{sp} growth is requested with the circumstance that at low droplets concentrations (for instance $< 2,9\%$), distance between droplets-dipoles become more, than 6 radius, i.e. at low concentrations forces of dipole-dipole attractions become neglecting small and separation in electric field does not work. Increasing of the E_{sp} between electrodes 5 create conditions for increasing forces F_D between small droplets at low concentrations.

So in the electrodes 5 and magnetic field area formed by winds 4, on the droplets affect the forces:
a) attraction forces, determined by dipole-dipole interactions between droplets by equation:

$$F_D = 6(|\alpha|)^2 E_o^2 \epsilon_{cp} / r^4, \quad (11)$$

As electrodes are settled on ferromagnetic rotor, they also rotate with it by asynchronous drive principle decreasing opportunity for chains of droplets formation between electrodes;

6) forces F_G of electric field E_o gradient $\text{grad}E$ by equation:

$$F_G = 2\pi\epsilon_o(\epsilon - 1)E_o R^3 \text{grad}E^2 / (\epsilon + 2), \quad (12)$$

where R – outer radius of electrode. Under this forces droplets and impurities will move along $\text{grad}E$ direction in the area of maximal field E_o .

b) forces F_L of Lorentz by equation:

$$F_L = q[\mathbf{v} \mathbf{B}] \quad (13)$$

where $\mathbf{B}$ – magnetic induction of alternating (rotating) magnetic field; $\mathbf{v}$ – linear velocity of magnetic field rotation. Here we observe move not of the droplets, but of the rotating magnetic field with velocity $\mathbf{v}$. Under effect of force F_L charged small droplets move down where their concentration is greater. Due to charge and dipole moment the droplets also aspire to move in the direction of magnetic field gradient $\text{grad}B$, i.e. to the sources of magnetic field 4 - to the perimeter of the block I, where droplets coalescence and precipitate.

3. Then purified water and oil through flow switchers III3 and III1 feed on the output (after block I) control in PMR-analyzer 9 for determination of water parameters.

Conclusions

With the object of operative control in the sole device, measurement range increasing and permanent flow analysis of all soiling of water by impurities we proposed the method of salts and oil determination on the base of pulse proton magnetic resonance, including excitation of protons spins in the sample, sited in constant magnetic field the spin-echo proton magnetic resonance signals by the

series of radiofrequency pulses, registration of their amplitudes A_i and relaxation times, using which the concentrations of salts and oil in water is determined.

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