

ORGANIC ACIDS SOLID PHASE EXTRACTION AS OIL TRACER AGENTS

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During the past years free organic acids (FOA) have become the main substance for the oil tracer monitoring. FOA are characterized by their poor biodegradability, traditional processing methods such as flocculation, chemical oxidation, and membrane separation are not suitable. Nevertheless, adsorption is shown to be potentially powerful because of its imaginable opportunity to design the chemical composition of the adsorbent surface. During oil field monitoring it is necessary to control organic acids content at level no less than half of maximum allowable concentration (MAC), i.e. $5 \cdot 10^{-3}$ mg/l. In almost any analysis method determining low concentration of analyte requires preconcentration, more often carried out by solid phase or liquid extraction. Within separation and concentration methods the solid phase extraction is widely applied because of its relative simplicity, usage of minimal organic solvent and high concentration factors. The study focuses on testing chelate containing sorbent on metal phthalocyanines for organic acids solid phase extraction from water solutions and on improving organic acids pretreatment when analyzing water samples.

Chelate containing sorbents were synthesized from phthalic anhydride urea, silica gel (Silipor 075) with bonded metal chloride [1, 2] and ammonium molybdate after heated up agitating at 2 °C/min up to 180°C into a reactor and after that held in isothermal conditions for 6 hours. Infrared spectroscopy on SPEKORD-75JR and thermal analysis on derivatograph Q-1500D were used to examine synthesis products.

Concentrating was carried out on 70 mm length and 4 mm in diameter steel for-column containing 0.7 g of Silipor 075 sorbent with chelate complex adsorption layer or equivalent amount of 0.8 g Oasis HLB sorbent.

Calculation of bonded metal atoms from wash solutions polarography data showed that as a result of chemical bonding there were $(2.6 \pm 3.0) \cdot 10^{21}$ metal atoms, which corresponds to scientific data on four hydroxyl groups for each Silipor surface nm². Derivatographic method also determined the amount of metal phthalocyanines formed after chemical bonding. There was high thermal stability of the complex bonded noticed, i.e. destruction begins at temperatures higher than 330 °C. Polymeric sorbent Oasis HLB (Waters) is N-vinylpyrrolidone and divinylbenzene copolymer and at the same time has hydrophilic and hydrophobic properties, combined inverted-phase and anion-exchange functions for solid phase extraction from water solution.

Usage of various metal phthalocyanines as modifying components changes initial sorbent acid-base properties. There were kinetic curves of metal phthalocyanines obtained to understand the influence of modifying additive on sorbent acid-base properties. Modified surface acid-base nature has most influence in organic acids sorption. Analysis of $\Delta pH_{10} = pH_{10} - pH_0$ values shows that there are Lewis acid sites on sorbents surface. pH values for CuPhC samples vary from 7.8 to 8.2, which is not significantly different from initial sorbent pH. At the same time Ni(II) and Co(II) phthalocyanines insertion changes pH value by more than 1.5 units. ZnPhC modified surface shows acid properties dominance.

The sorption concentrating was carried out with chelate containing sorbents in comparison with standard Oasis HLB polymeric sorbent and liquid extraction, which is usually used for similar pretreatment (Tables 1, 2).

Table 1

Results of FOA HPLC determination with varying concentration methods

Acids	Inserted, µg/l	Identified, µg/l			
		LE	Oasis HLB	ZnPhC	NiPhC
3-Organic	1.5	1,2±0,2	1,5±0,1	1,3±0,2	1,5±0,1
4-Organic		1,3±0,2	1,5±0,1	1,4±0,2	1,5±0,1
3-Organic	20.0	18.0±2.0	20.0±1	18.0±3.0	20.0±1.0
4-Organic		20.0±2.0	20.0±1.0	18.0±2.0	20.0±1.0
3-Organic	60.0	61.0±5.0	60.0±3.0	56.0±5.0	60.0±2.0
4-Organic		63.0±5.0	60.0±3.0	55.0±6.0	60.0±2.0

Table 2

FOA extraction ratio, %

Acids	LPE	Oasis HLB	ZnPhC	NiPhC
3-Organic	74±2	81±3	79±3	84±4
4-Organic	69±2	77±2	76±3	81±4

Chelate containing sorbents allow sorbing organic acids more effectively than Oasis HLB, because of specific intermolecular interactions of electron-donor oxygen atoms in sorbates functional groups and metal acceptor ions in chelates. Organic acids, prone to donor-acceptor interaction as electron pair donor, retain more strongly in chelate complexes than on Oasis HLB electron-donor surface because they form associate with electron-deficient part of metal complex.

Sorbent with Cu phthalocyanine shows selectivity towards FOA, which is due to sorption through selective complexation of electron-deficient chelate parts in adsorbed layer with nucleophilic substances. It is the most efficient variant

to use this sorbent for organic acids preconcentration from water solutions with following HPLC determination because it displays stability under water vapour influence.

Zn phthalocyanines sorbs FOA less effectively compared to Ni phthalocyanines, which is due to partial destruction of a bond with the complex surface during methanol desorption. In eluting mix through sorbent containing Zn phthalocyanine, the latter shatters, and the longer the process, the less it is possible to model analysis results.

Minimal FOA concentration, which can be determined in model solution at standard concentrating procedure, is 3×10^{-5} mg/l. It is possible to use metal phthalocyanines as sorbents during organic acids extraction from water solutions. HPLC methods with preconcentration are proposed to evaluate organic acids by means of solid-phase extraction on a sorbent with a surface layer of Cu phthalocyanines with extraction effectiveness of 78 %.

References

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WATER CONTROL TECHNOLOGY FOR PRODUCTION WELLS

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Unwanted water production is a major challenge for oil and gas wells. Problems arise when water production exceeds the economic level (water/oil ratio). In this case, oil production is almost unprofitable [3]. Produced water can be divided into two types. The first type includes water coming from injection wells or active aquifers that contribute to oil displacement from a reservoir. The second type includes water coming to a well and produced without oil or with oil output insufficient to cover water disposal costs. Water of the second type can occur in a particular well for a variety of causes. Table 1 shows a simplified classification of problems, although they may occur in more combinations in practice [2].

Table 1

Classification of Problems Associated with Excess Water Inflows

Problem	Cause:	Solutions for wells	
		Vertical	Horizontal
1. Leaks of casing, tubing or packer	- aging wells - technological reasons - corrosion	- use of insulating fluids, plugs, cement bridges, and packers - use of casing patches	
2. Leakage behind casing	- low-quality cement sheath - voids in casing annulus	- use of insulating plugging fluids	
3. Oil-water contact (OWC) movement	- very low vertical permeability	- plugging lower perforation holes using mechanical systems	- horizontal sidetracking
4. Watered interval without flows between layers	- a highly permeable interval, bounded by aquitards from above and below	- using inelastic insulating fluids or mechanical insulators	- this problem does not affect horizontal wells drilled only to a producing reservoir
5. Fractures or faults between injection and production wells	- fractured or porous-fractured reservoirs, branched fracture networks	- injection of gels - water shut-off (the best solution to this problem)	

This problem is typical for oil and gas fields at late development stages. It leads to loss of productivity, higher cost of oil and increased well water-cut. One of the ways to solve this problem is to conduct water shut-off treatment in oil and gas wells by injecting chemicals that can be filtered into a porous medium and plug pathways of unwanted water into the well [2].

There are a lot of chemicals that can be used for water shut-off treatment, but the final choice depends on the cause of water production, a place from which water comes, and petrophysical parameters of a producing reservoir. However, most water shut-off materials were found to be ineffective in field tests.

Chemical water shut-off must provide the following results:

- injected chemicals must completely fill water pathways;
- the chemicals must create a water barrier that ensures sufficient resistance in subsequent well operations without being destroyed under current depression conditions;
- water shut-off treatment must not deteriorate flow properties of the oil-saturated portion of the reservoir;

In this case, chemicals and solutions must:

- be chemically inert to rocks and pipe metal;
- be cheap and commercially available;
- guarantee not only high efficiency of shut-off treatment, but also safety at work;
- comply with applicable environmental requirements;