

# Behavior of Oil – Aqueous Solution Systems in Rotating Coil Column

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## Abstract

Behavior of oil–aqueous solution systems used for oil analysis in rotating coil column (RCC) has been studied. An RCC can be used as effective tool for pre-concentration and isolation of trace metals from crude oil and oil products into acidic solutions. An oil sample is continuously pumped through column as a mobile phase whereas an aqueous acidic solution is retained in the column as a liquid stationary phase. The main dependences of the stationary phase retention on construction and operating parameters as well as on the physicochemical properties have been investigated. Optimal values of density and viscosity of crude oil and oil products that could be analyzed with an RCC were estimated. Theoretical dependences of the stationary phase retention on density and viscosity differences between stationary and mobile phases were obtained. These studies allow predicting the retention of the different oil/oil product–aqueous solution systems in an RCC.

**Keywords:** An RCC; Oil analysis; Stationary phase retention; Rotating coil columns

## Introduction

Trace elements detection in crude oil and oil products is a very difficult analytical task. Information about trace elements concentration is increasingly important not only for oil production and refining technology, but also for characterization of crude oil types, for fixing theirs prices and for reconnaissance investigations [1–3].

Abilities of the liquid stationary phase retention during pumping of oil samples through column enable isolation and pre-concentration of the inorganic impurities into acidic aqueous solutions. In this case an RCC can be used as a tool for the sample pretreatment and preparation. Therefore, preliminary investigation on retention features of oil/oil products – an aqueous phase system in an RCC is very important for solving practical analytical problems [3, 4].

The stationary phase volume retained in an RCC is characterized by  $S_{\rm f}$  factor (ratio of the stationary phase volume  $V_{\rm S}$  to the total column volume  $V_c$ ). It is well known that value of  $S_t$  depends on the parameters of a coil planet centrifuge (rotation and revolution radii, tube internal diameter), on the operating conditions (rotation and revolution speeds, flow rate and direction of mobile phase pumping), and the physicochemical properties of the two-phase organic-aqueous systems used. It should be mentioned that the influence of coil planet centrifuge parameters and operating conditions on the stationary phase retention are rather well studied for two-phase liquid systems used for organic and inorganic separations. A number of papers, describing the influence of the physicochemical parameters of two-phase liquid systems (interfacial tension, polarity of solvents, difference in the densities and viscosities of the phases, time of phase separation, and the length of capillary waves at the phase boundary) on the retention of the stationary phase in a column, have been published [5-16]. So far, stationary aqueous phase retention in oil-aqueous solution systems has not been investigated. Analyzed oil samples are characterized by a great number of components and high viscosity.

Effects of hydrodynamic parameters and physicochemical properties of two-phase systems on the retention of aqueous stationary phase should be investigated. Preliminary studies have shown that physicochemical properties of two-phase systems of analyzed oil are determinative and influence the retention factor of the stationary phase in a column [3]. Optimal rotation speeds, flow rate and direction of sample pumping, density and viscosity of the crude oil and oil products that could be analyzed by an RCC should be estimated. This data will allow predicting the retention of various oil/oil product–aqueous solution systems in an RCC column. That was shown on the several mixed oil products samples (with different  $\rho$  and  $\eta$ ) and 9 consequent oil distillates with different boiling points.

Data obtained is helpful for finding optimal conditions of extraction and high metal recoveries. Trace metals are concentrated into the stationary aqueous phase and then easily determined by ICP-MS. The proposed method of pre-concentration of trace elements from oil has no analogues.

## Materials and Methods

## Instruments

RCC experiments were performed with "Spring-3M" J-type single layer synchronous horizontal planetary centrifuge (made in the Institute for Analytical Instrumentation St. Petersburg, Russia) with a total column volume of 19 ml at constant T = 20°C. RCC coiling diameter was 120 mm, revolution radius 93 mm, length of the Teflon<sup>\*</sup> tube 1.15 m. Phases were pumped through an RCC using a peristaltic pump (Masterflex, UK). The planetary centrifuge and peristaltic pump are shown on Figure 1. All working parameters for the planetary centrifuge are given in Table 1.

An RCC was filled with deionized water or aqueous acid solution in stationary mode. Then the planetary centrifuge is set to rotate and the mobile phase (oil or diesel) was pumped through the column. Optimal elution mode when the lighter phase is pumped from tail to head was shown for amount of biphasic organic systems [5-16]. The acid solution

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is retained in a hydrodynamic column due to a complex centrifugal field while the mobile oil phase was pumped through the column. After the run, water or acid solution was pumped out of the non rotating column.

 $S_{\rm f}$  values were measured after 2 volumes of column of the mobile phase were pumped through primarily full of aqueous phase planetary centrifuge.

Samples densities ( $\rho$ ) were measured using KEM DE40 densimeter (Japan) at 20 °C. Viscosities ( $\eta$ ) were measured with HVN 472 Herzog multi-range viscometer (Germany) at 20 °C with preheating at 60 °C, if necessary.

All experiments were performed in 5 repetitions. Mean quantities are listed throughout.  $S_f$  values have < 5% divergence of results.

### **Reagents and materials**

High purity de-ionized water (resistivity 18.2 m $\Omega$ ) obtained from a Milli-Q water purification system (Millipore, Canada) was used throughout. Ultra pure nitric acid (Merck, Germany) was used for preparing of the acidic solutions.

All experiments in an RCC for the  $S_{f}$  evaluation were performed with deionizer water and HNO<sub>3</sub> solutions as the stationary phase.

Toluene, isooctane and acetone of chemically pure grade were used for column rinsing. After each experiment 70-100 mL of every solvent were pumped through non rotating column for cleaning.

Oil and oil products samples with different physicochemical properties were used for retention studies. Their compositions, densities and kinematic viscosities are shown in Table 2.

# **Results and Discussion**

### Retention of aqueous stationary phases

Effect of hydrodynamic parameters and physicochemical properties of crude oil and oil products used as a mobile phase on the volume of the stationary phase (acidic aqueous solution) retained in an RCC was studied. Preliminary researches [3, 4] have shown that applying diluted aqueous solutions enables isolation of the most metals from oil by an RCC. Therefore deionized water or diluted acidic solutions were used as the stationary phase. This investigation was necessary for the development of new methods of pre-concentration and isolation of the inorganic impurities from different oils.



Figure 1: Photo of "Spring-3M" planetary centrifuge.

Column	Stationary	Rotating	Beta	Mobile phase	Tube
volume	phase volume	speed	ratio	flow rate	diameter
V <sub>c</sub> , cm <sup>3</sup>	V <sub>s</sub> , cm <sup>3</sup>	ω, rpm	β = r/R	<i>F</i> , mL/min	<i>d</i> , mm
19	1-19	100-1000	0.65	0.2-1.2	0.8, 1.2

Table 1: Working parameters for the planetary centrifuge.

Sample	Δρ, g/cm <sup>3</sup>	∆η, cSt (×10 <sup>-6</sup> m²/s)		
100%ª	0.206	1.27		
75% (v)ª + 25% <sup>b</sup>	0.177	3.02		
60% <sup>a</sup> + 40% <sup>b</sup>	0.161	5.33		
50%ª + 50% <sup>b</sup>	0.154	6.68		
100% <sup>b</sup>	0.094	51.4		
100%°	0.227	0.51		
75% (v) <sup>c</sup> + 25% <sup>d</sup>	0.179	2.78		
60% <sup>c</sup> + 40% <sup>d</sup>	0.158	4.97		
50% <sup>c</sup> + 50% <sup>d</sup>	0.147	6.96		
100% <sup>d</sup>	0.065	74.6		
Sample	ρ, g/cm³	η, cSt (×10 <sup>-6</sup> m²/s)		
Deionized water	0.998	1.01	Stationary phase	
0.5 M HNO, solution	1.05	1.41		
Hexane	0.655	0.294	Organia achranta	
Isooctane	0.688	0.503	Organic solvents	

iengizskaya oli - a, residual fuel oli - b, petrol AI-95 - c, lubricating oli - d

 Table 2: Physicochemical parameters for test samples, mixed test samples, stationary phases and organic solvents.

## Effect of hydrodynamic parameters

It was found that behavior of various types of oils in an RCC is very different [3,4] some oil – aqueous solution systems did not retain in a column or gave stable emulsions. Density and viscosity of the mobile phase (oil product) are very important parameters which in most cases determine the needed direction of this phase pumping through the column. Pumping direction of a lighter phase as a mobile (oil products or oil have lower density then the stationary phase) from the top to the bottom of an RCC is optimal for the biphasic systems used. Otherwise aqueous phase could be displaced by oils.

Experimental dependences of the stationary phase retention on column rotation speeds and flow rates of the mobile phase were obtained.

It should be noticed that increase of  $\omega$  with constant flow rate (1 mL/ min) leads to increase of  $S_f$  value up to 0.95. This effect was observed on all samples tested (Table 3). Model dependences of stationary phase retention for the hydrophobic biphasic systems have been formulated [14]. That theoretical dependence of  $S_f$  on rotating speeds under 800 rpm for two-phase liquid systems has the same view as for oil-water systems studied. Experimental  $S_f$  dependence on the column rotation speeds at F = 1 mL/min for Tengizskaya oil – water system is shown in Figure 2. Theoretical  $S_f$  dependence on the column rotation speeds (at constant F) for the hydrophobic biphasic systems is shown in Figure 3. Besides, higher rotating speeds cause emulsion on the oil-water interface and decrease  $S_f$  value.

There is no retention of the stationary phase at  $\omega < 200$  rpm in oil – aqueous solution systems.  $S_f$  less than 0.1 (looks like segment I in Figure 3). At  $200 < \omega < 700$  rpm the increase of  $S_f$  up to 0.95 could be observed (segment II). Some emulsion formation (on the oil-water interface) at  $\omega$  lower than 600 rpm was also observed. Emulsification was observed for all oil and oil products studied. This leads to decreasing of  $S_f$  values too. As it sighed before higher rotation speeds (over 800 rpm) cause the stratification of the analyzed oil samples. It was crucial for samples with high viscosity (Table 1). This leads to blocking of the RCC tube and decreasing of  $S_f$  value. Disadjustment of the theoretical model for the hydrophobic biphasic systems [15] and experimental data at segment III is clearly seen. This feature of the multiphase oil systems could enable to find optimal column rotation speeds to obtain high  $S_f$  values. Therefore  $\omega = 750$  rpm was chosen for most of the experiments allowing to work with high  $S_f$  without any emulsions on oil-water interface.

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Dependence of  $S_f$  on flow rates of the mobile phase is linear (Figure 4). In the meantime we have not yet used large range of flow rate values. Increasing of F value is inexpedient in cause of decreasing of phase contact time and mass transfer. Decreasing of F leads to increasing of analysis time. That is especially crucial for concentrating metals from oil. It should be noticed that decrease of the mobile phase flow rates (F) does not increase  $S_f$  values greatly. Therefore F = 1 mL/min was used throughout.

Influence of  $S_f$  on internal diameter of the tube used as a column was also determined. It was shown that tubes with bigger *d* promote increasing of  $S_f$  value. As an example, changing of the internal diameter from 0.8 to 1.2 mm leads to increase of  $S_f$  values from 0.5 to 0.73. This effect was observed for diesel oil–water system at constant  $\omega = 750$  rpm and F = 1 mL/min. Similar effect was observed in several studies [8, 14, 16]. The same  $S_f$  values for the RCCs with bigger *d* could be obtained at lower rotation speeds.

#### Effect of physicochemical properties

The first attempt to correlate the stationary phase retention and physicochemical properties of liquid systems was made by Berthod et al. [9]. It was reported that the value of  $S_f$  increased linearly with











Sample	Δρ, g/cm <sup>3</sup>	Δη, cSt (×10 <sup>-6</sup> m²/s)	S <sub>f</sub>
100% <sup>a</sup>	0.206	1.27	0.95
75% (v) <sup>a</sup> + 25% <sup>b</sup>	0.177	3.02	0.82
60% <sup>a</sup> + 40% <sup>b</sup>	0.161	5.33	0.57
50% <sup>a</sup> + 50% <sup>b</sup>	0.154	6.68	0.24
100% <sup>b</sup>	0.094	51.4	0
100% <sup>c</sup>	0.227	0.51	0.98
75% (v) <sup>c</sup> + 25% <sup>d</sup>	0.179	2.78	0.89
60% <sup>c</sup> + 40% <sup>d</sup>	0.158	4.97	0.55
50%° + 50%d	0.147	6.96	0.16
100% <sup>d</sup>	0.065	74.6	0
Fraction 180-200	0.197	0.483	0.79
F200-220	0.188	0.937	0.76
F220-240	0.179	1.41	0.72
F240-260	0.170	2.17	0.64
F260-280	0.162	3.66	0.52
F280-300	0.152	5.95	0.39
F300-320	0.143	9.14	0.22
F320-340	0.137	13.9	0.09



**Table 3:** Physicochemical parameters and  $S_{t}$  for test samples. Marked samples (grey filling) were used to compare theoretical and experimental  $S_{t}$  values.

an increase of the density difference between the two phases ( $\Delta \rho$ ). We have earlier shown for saturated hydrocarbons - water systems that the retention factor of stationary phase in a column decreased with decreasing difference between the viscosities of the phases [1,16]. The greater the difference between the viscosities of the phases, the better an organic solvent of this type is retained in the column.

Behavior in an RCC of 19 samples with different physicochemical properties was investigated. Compositions, densities and kinematic viscosities of these samples and  $S_f$  values (of the stationary phase for oil product–deionized water systems) are shown in Table 3.

Figure 5 illustrates experimental data (dots) and approximation line for retention of 15 samples in an RCC. These experiments with oil/oil products – water systems show a nonlinear (sigmoidal)  $S_f$  dependence on  $\Delta\rho$  of mobile and stationary phases. Figure 5 also demonstrates that increasing of  $\Delta\rho$  leads to increasing of  $S_f$  value. Statistic calculations of the experimental data allow revealing dependences of  $S_f$  on  $\Delta\rho$  at constant  $\omega$  and F (Table 3):

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$$S_{f} = 0.903 - \frac{0.920}{1 + \exp(\frac{\Delta \rho - 0.158}{0.0106})}, R^{2} = 0.995$$
 (1)

where R is a correlation coefficient.

Behavior of 4 independent samples (Table 3) in an RCC was studied in order to check the accuracy of the suggested fit. Figure 6 and Table 4 show good correlation between experimental  $S_f$  results for 4 independent samples and sigmoidal approximation (1) for 15 samples.

Figure 7 illustrates experimental data (dots) and approximation line for retention of 15 samples in an RCC. These experiments with oil/oil products – water systems show a nonlinear (exponential decay)  $S_f$  dependence on the viscosity difference between the two phases ( $\Delta\eta$ ) of mobile and stationary phases. Figure 7 also demonstrates that increasing of  $\Delta\eta$  leads to increasing of  $S_f$  value. Statistic calculations





Sample	$\Lambda \boldsymbol{\rho}$ . g/cm <sup>3</sup>	∆ <b>n</b> . mm²/s	S.(experimental)	<b>S</b> .(1)	<b>S</b> .(2)
		,			-+(-)
100%ª	0.206	1.27	0.95	0.91	0.89
60%ª + 40%	0.161	5.33	0.57	0.53	0.52
100% <sup>b</sup>	0.094	51.4	0	0.01	0
Fraction 320- 340	0.137	13.9	0.09	0.12	0.13
Tengizskava oil - a. residual fuel oil – b					

 $S_{\ell}(1) = 0.903 - \frac{0.920}{0.920}$ 

$$= 0.903 - \frac{1}{1 + \exp(\frac{\Delta \rho - 0.158}{0.0106})} \text{ and } S_f(2) = 0.973 \cdot \exp(-\frac{\Delta \rho}{6.95})$$

**Table 4:** Experimental and theoretical  $S_{f}$  values at  $\omega$  = 750 rpm and F = 1 mL/min.



of the experimental data allow revealing dependences of  $S_f$  on  $\Delta \eta$  at constant  $\omega$  and *F* (Table 3):

$$S_f = 0.973 \cdot \exp(-\frac{\Delta \eta}{6.95}), R^2 = 0.991$$
 (2)

where R is a correlation coefficient.

Behavior of 4 independent samples in an RCC was studied in order to check the accuracy of the suggested fit. Figure 8 and Table 4 show a good correlation between experimental  $S_{\rm f}$  results for 4 independent samples and exponential approximation (2) for 15 samples.

Formulas (1) and (2) could be used for estimation of limit values of  $\Delta \rho$  and  $\Delta \eta$  and prediction of the systems behavior in an RCC. Limit values of  $\Delta \rho$  and  $\Delta \eta$  could be expressed as follows:

At such values of  $\Delta \rho = 0.109 \text{ g/cm}^3$  and  $\Delta \eta = 25.6 \text{ mm}^2/\text{s}$  stationary phase does not retain in an RCC ( $S_i = 0$ ).

When  $\Delta \rho$  is higher than 0.210 g/cm<sup>3</sup> and  $\Delta \eta$  is less than 0.470 mm<sup>2</sup>/s the stationary phase retention is higher than 90% ( $S_{\rm f} > 0.9$ ).

Theoretical dependences of the stationary phase retention that has been mentioned above allow predicting behavior of the oil/oil products – aqueous solutions systems in an RCC. Limit and optimal values of density and viscosity of the analyzed sample could be calculated by formulas (1) and (2). It was shown that oil/oil products with  $\rho < 0.90$  g/cm<sup>3</sup> and  $\eta < 7.5$  mm<sup>2</sup>/s are suitable for analysis in an RCC without any additional preparation steps. Oil/oil products with higher values

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of  $\rho$  and  $\eta$  should be doped or diluted with low density and viscosity ultrapure solvents (such as 2, 2, 4-trimethylpentane (isooctane) or hexane – Table 2). Sufficient  $S_f$  of 0.5 M HNO<sub>3</sub> solution is 0.25 for isolation of trace elements from oil.

It should be mentioned that complexing agents (EDTA, methylamines and etc.) could be added to the stationary phase in order to increase metals recoveries. That will cause changes of density and viscosity of the aqueous solutions, where  $\Delta \rho$  and  $\Delta \eta$  values change accordingly. Using formulas (1) and (2) requirements for the stationary and mobile phases could be expressed as follows:

When  $\Delta \rho$  is higher than 0.15 g/cm<sup>3</sup> and  $\Delta \eta$  is less than 9 mm<sup>2</sup>/s the stationary phase retention is higher than 25% ( $S_{\rm f} > 0.25$ ).

# Conclusion

An RCC can be used as an effective method for pre-concentration and isolation of trace metals from the crude oil and oil products. An oil sample is continuously pumped through RCC column as a mobile phase whereas an aqueous acidic solution is retained as a liquid stationary phase. Effects of hydrodynamic parameters and physicochemical properties on the retention of aqueous stationary phase were studied. Investigations have shown that physicochemical properties of the analyzed oil are determinate and influence the retention factor of the stationary phase in a rotating coil column. Theoretical models of the retention of the aqueous solutions in oil-water systems were suggested. These dependences helped to find optimal values of density and viscosity of crude oil and oil products that could be analyzed with an RCC. Retention in oil/oil product - aqueous solution systems in a rotating coil column could be predicted. Data obtained enables to find optimal extraction conditions for high metal recoveries. Acceptable hydrodynamic  $\omega$  = 750 rpm and *F* = 1 mL/min parameters allow to work with high  $S_f$  (for oil/oil product – aqueous phase systems) without any emulsions on oil-water interface. Besides, requirements for the stationary and mobile phases of such systems could be formulated as: S<sub>f</sub> > 0.25 when  $\Delta \rho$  > 0.15 g/cm<sup>3</sup> and  $\Delta \eta$  < 9 mm<sup>2</sup>/s.

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