

THE POSSIBILITIES OF EXTRACTION APPROACH FOR RECOVERING OF METALS FROM OIL PRODUCTS

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Abstract

The extraction approach for recovering of trace elements from oil/oil products are proposed in this work. It has been shown that most of elements are extracted from oil/oil products to mineral acids solutions. Extraction degree of most valuable metals during the process varies from 75 to 90%. The proposed method could be used as a new cheap, precise and time saving analytical method (as compared to standard methods) of elemental analysis of the oil and the approach for development of effective technology for metal recovery from organic matrices.

Key words: extraction, demetallization, concentration, oil products, heavy oil

1. INTRODUCTION

Rising energy prices and depleting resources of conventional crude oil are turning attention toward the vast global resources of heavy oil, extra heavy oil, and bitumen. Heavy oil is estimated to account for nearly 50% of total remaining global recoverable oil resources, with 2.0 trillion barrels of heavy oil and 2.3 trillion barrels of conventional oil recoverable for future production (Silverman 2011). Increase the density of crude oil is accompanied by a rapid increase the amount of metal-containing compounds in its composition (Banerjee 2012) Depending on the origin of crude oil, concentration of metals may exceed 1000 ppm (Ali 2006). It is considered that the elements contained in the oil in trace amounts, may exist in the form of a fine aqueous salt solutions, suspensions of fine mineral rocks, as well as chemically bonded with organic substances or complex molecular compounds. Vanadium and nickel are most studied metals of the variety of metals contained in the oil. This is due to the fact that they are present in the oils in relatively high concentrations, and almost completely concentrated in the asphaltene-resinous fractions, i.e. in fractions boiling at a temperature above 350°C. It is found that up to 50% of nickel and vanadium contained in oil exist as porphyrin complexes. It is assumed that the data are metalloporphyrins and the biogenic origin were formed by metal exchange reactions of the metabolic and animal pigments (or) of plant origin, such as hemoglobin and chlorophyll. The total content of trace elements in oils, on average decreases with increasing depth and age of the sediments. It has been established that the metal part is a part of resin-asphaltene substances in the form of salts of organic acids and chelates, the other bulk - metal complex as a polydentate complexes.

On the one hand the presence of large amount of metals in the feedstock is one of the major problems during refining of heavy oil and residuum fractions, since they cause rapid catalyst poisoning due to deposition on catalyst surface that is followed by active site coverage and pore mouth constriction/blockage (Ancheyta 2013). On the other hand rare and rare earth metals in the composition of heavy oil feed are valuable associated components. Recovery of metals from oil can increase the profitability of oil production and refining and provide metallurgical industry by additional raw materials.

As a result, in recent years increasing attention is being paid to the problems of metal removal from heavy oil feedstock. As is known, demetallization and concentration of metals can be achieved in various processes of treatment and refining of petroleum feedstocks, including mass transfer processes, thermal and catalytic methods, electrochemical treatment and etc. (Ali 2006). Extraction processes are among the more promising methods for separation and remove of metals due to technological

simplicity, flexibility and relatively low capital and operating costs as compared to thermal conversion processes. The extraction efficiency in this case depends mainly on a proper selection of operating conditions and a proper choice of solvent and/or extractant (Al-Sabawi 2011). At this study the applicability of multistep extraction procedure for demetallization of oil/oil product samples is considered. The multistep extraction process was realized by use the planetary centrifuge with rotating coiled column (RCC). Method of substances separation based on the using of RCC called countercurrent chromatography (CCC) and was invented at the beginning of 60s. One of the phases (stationary) is retained in RCC with no solid supporter or adsorbent due to activity of mass forces, which appear upon the rotation of a column around its own axis and, simultaneously, its revolution around the central axis of the apparatus (planetary centrifuge), while the second phase (mobile) is constantly pumped through the system. Almost any two-phase liquid system consisting of two immiscible phases can be used as a liquid system for the countercurrent chromatography. CCC is used for the preconcentration and separation of trace elements in the analysis of complex multicomponent solutions (Maryutina 1999). The variation of the phase composition in the experiment allows the change of the distribution coefficients for the sample components to be determined, which, in its turn, makes possible the preconcentration of elements in the stationary phase and the removal of matrix species with the flow of the mobile phase (Berthod 2009).

2. MATERIALS AND METHODS

2.1. Reagents and samples. For preparing extraction reagent (0.5 M HNO₃) we used high purity deionized water (resistivity 18.2 mΩ) obtained from a Milli-Q water purification system (Millipore, Canada), as well as ultrapure nitric acid HNO₃ (Merck, Germany). In the quantitative elemental analysis by ICP-MS we prepared standard solutions by diluting multielement Agilent standards A (Al, As, Ba, Be, Bi, B, Cd, Ca, Ce, Cs, Cr, Co, Cu, Dy, Er, Eu, Gd, Ga, Ho, In, K, Fe, La, Li, Lu, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, Rb, Re, Sm, Sc, Se, Sr, Tb, Th, Tl, Tm, U, Yb, Y, V, Zn 10 μg/mL ± 0.5% in 2% HNO₃) and B (Ag, Ge, Hf, Mo, Nb, Sb, Si, Sn, Ta, Te, Ti, W, Zr 10 μg/mL ± 0.5% in 2% HNO₃ + TrHF). In the quantitative elemental analysis by direct input of oil solution to ICP-AES we prepared standard solutions by toluene diluting a reference sample (Conostan) with a concentration 900 μg/g for each element (V, Cr, Ni, Cu, Zn, Pb) in the form of cyclohexanebutirates in light oil. Elements concentration range for all the elements was 1-100 μg/L. Calibration coefficients of determination for all elements were 0.9994-0.9999. All the experiments on demetallization were performed with light oil (Tengizskaya, gas condensate) with density $\rho = 0.795$ g/mL and viscosity $\eta = 1,504$ mm²/s, heavy oil residue from Chernigovskaya oil with density $\rho = 1,008$ g/mL and viscosity $\eta = 857$ mm²/s and oil sample obtained by mixing of West-Siberian, Tatar and Bashkir oils with density $\rho = 0.860$ g/mL.

2.2. Multistep extraction process in RCC. Figure 1 schematically illustrates a type J single layer synchronous planetary centrifuge. The column is formed by winding Teflon tubing around a cylindrical holder. The column holder rotates around its own axis and revolves around the centrifuge axis at the same speed (ω) and in the same direction (rotating end revolution speeds in this experiment were 750 rpm). An aqueous solution is retained in column due to the complex gravitational (centrifugal) field while the mobile phase (oil) is pumped through the column. RCC experiments were performed with "Spring-3M" vertical planetary centrifuge (Figure 2) made in the Institute for Analytical Instrumentation St. Petersburg, (Russia) with a total RCC volume (V) of 19 mL. Peristaltic pump (Masterflex, UK) was used for the mobile phase flow (flow rate $F = 1$ ml/min). Teflon tube-column was used through all the experiments. After the experimental run, the acid solution was pumped out of the nonrotating column and analyzed by ICP-MS. Toluene, iso-octane, and acetone of chemically pure grade were used for column rinsing. After every RCC experiment 70-100 of each solvent were pumped through the stationary column.

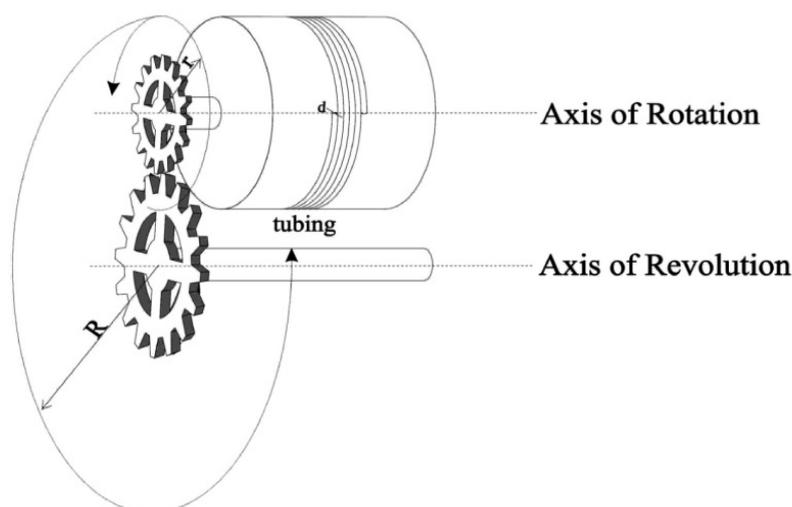


Figure 1. Scheme of planetary centrifuge, where r is spool radius and R is rotor radius



Figure 2. Planetary centrifuge “Spring-3M”

2.3. Autoclave Decomposition. To compare results of RCC elements isolation from oil with other techniques, autoclave decomposition of oil samples was used. Module “MKP-04” with autoclave NPVF “ANKON-AT-2” (Russia) was used for decomposition in a closed system. Oil samples were digested by concentrated ultrapure HNO_3 in sealed Teflon containers, than cooled and diluted to 50 mL by deionized water (washing of containers sides). Total heating time of oil sample at different temperature conditions takes 4 h. These diluted samples were analyzed by ICP-MS.

2.4. Heavy oil residue lysing. Samples of heavy oil residue (HOR) were heated in an oven at 100 degrees. After that a weighed sample of 1 g was transferred to a flask of 100 ml, was added to 60 ml of solvent (toluene), and thoroughly stirred on a shaker for 15 minutes.

2.5. ICP-MS Determination. ICP-MS measurement was performed using spectrometer Agilent 7500c (U.S.). All ICP-MS data (final concentrations in analyzed solutions, calibrations, tunes, statistics, etc.) was obtained from ICP-MS Top Agilent program pack.

2.6. *ICP-AES Determination.* ICP-AES measurement was performed using spectrometer iCAP 6500 Duo with an ISOMIST accessory (Thermo Scientific, U.S.). All ICP-MS data (final concentrations in analyzed solutions, calibrations, tunes, statistics, etc.) was obtained from ICP-AES program pack.

3. RESULTS AND DISCUSSION

The aqueous solution of nitric acid was chosen as the extraction solution to extract metals from the oil using a multi-stage extraction because it is provided high values of distribution coefficients for different elements from organic mediums and minimized of interferences during ICP-MS measurement. Influence of nitric acid concentration on recovery for inorganic elements from oil have been preliminary investigated (Maryutina 2009). The optimal concentration of nitric acid solution (0.5 M) for trace element recovering from oil was chosen in preliminary studies too (Maryutina 2009). The results of ICP-MS analysis of the extracts and obtained after autoclave decomposition of the sample were compared to assess the effectiveness of the oil demetallisation process.

Table 1 provides comparative data of elemental analysis of Tengizskaya oil using autoclaves decomposition and RCC extraction. All measurements were conducted by ICP-MS. The metals concentrations in oil obtained by RCC extraction are higher than concentrations of the same metals obtained with other method except V and Cr. Autoclave decomposition allows detection of higher V and Cr concentrations. It could be explained by high binding energy of those metals in metalorganic compounds and, as consequence, higher solubility in the oil phase than in the aqueous acid solutions used. Currently the composition of stationary phase cannot provide the recovery of V and Cr from oil as required.

Table 1. Results of trace elements determination ($\mu\text{g/g}$) in Tengizskaya oil (ICP-MS detection method) (Maryutina 2009)

Isotope / Element	Autoclave decomposition ¹	Extraction in RCC ²
²⁷ Al	< DL	3.2 ± 0.6
⁵¹ V	0.06 ± 0.01	0.04 ± 0.01
⁵³ Cr	0.69 ± 0.14	0.06 ± 0.01
⁵⁸ Fe	< DL	0.017 ± 0.003
⁵⁹ Co	0.006 ± 0.01	0.014 ± 0.003
⁶⁰ Ni	< DL	0.014 ± 0.003
⁶³ Cu	< DL	1.3 ± 0.3
⁶⁶ Zn	0.14 ± 0.03	7.5 ± 1.5
²⁰⁸ Pb	0.08 ± 0.02	2.4 ± 0.5
Time for analysis	~ 6 h	~ 1 h

DL – Detection Limit

¹ Sample (oil) mass - 0.5 g, ² Sample (oil) volume - 52 mL.

Table 2 shows the results for the extraction of metals from oil sample obtained by mixing of West-Siberian, Tatar and Bashkir oils. Higher concentrations for most components, except for Al, V, and Ni, were found in the extracts, which confirms the results obtained for a Tengizskaya oil sample.

Table 2. Results of trace elements determination ($\mu\text{g/g}$) in mixing oil sample (ICP-MS detection method)

Isotope / Element	Autoclave decomposition ¹	Extraction in RCC ²
²⁷ Al	0.34 ± 0.07	0.16 ± 0.03
⁵¹ V	67 ± 5	0.13 ± 0.01
⁵³ Cr	< DL	0.015 ± 0.002
⁵⁸ Mn	< DL	0.056 ± 0.004
⁵⁹ Co	0.050 ± 0.003	0.095 ± 0.005
⁶⁰ Ni	18.1 ± 3.2	0.068 ± 0.004
⁶³ Cu	< DL	0.038 ± 0.003
⁶⁶ Zn	< DL	0.78 ± 0.08
²⁰⁸ Pb	< DL	0.078 ± 0.005
Time for analysis	~ 6 h	~ 1 h

DL – Detection Limit

¹ Sample (oil) mass - 0.5 g, ² Sample (oil) volume - 55 mL.

Table 3 shows the same regularities for heavy oil residue. Autoclave decomposition allows detection of higher V and Ni concentrations, but results obtained for other elements are comparable. It was necessary to convert a sample of heavy oil residues into a solution to be able to highlight the metals recovery using RCC (see. P. 2.4.).

Table 3. Results of trace elements determination ($\mu\text{g/g}$) in Chernigovskaya heavy oil residue using different pre-treatment procedure (ICP-MS detection method)

Isotope / Element	Autoclave decomposition ¹	Extraction in RCC ²
²⁷ Al	2.9±0.4	3.8±0.6
⁵¹ V	27±2	< DL
⁵³ Cr	0.9±0.2	1.1±0.2
⁵⁸ Fe	< DL	16±3
⁵⁹ Co	< DL	< DL
⁶⁰ Ni	30±5	0.9±0.4
⁶³ Cu	1.4±0.3	0.5±0.1
⁶⁶ Zn	< DL	2.8±0.5

DL – Detection Limit

¹ Sample (oil) mass - 0.5 g, ² Sample (oil) mass – 1.0 mL.

The fullness of elements transition to the aqueous acid solution by analyzing the HOR solution before and after extraction in RCC was studied. Table 4 shows the results of determination of Chernigovskaya oil residue element content before and after extraction in RCC, obtained by direct input to ICP-AES.

Accordingly these data almost all metals except Ni and V could be recovered from oil sample by using multistep extraction in RCC.

Table 4. Results of trace elements determination ($\mu\text{g/g}$) in Chernigovskaya heavy oil residue before and after trace element extraction using RCC and results of trace element determination ($\mu\text{g/g}$) in obtained nitric acid extract

Element	Before extraction in RCC (HOR) ¹	After extraction in RCC (HOR) ¹	After extraction in RCC (0.5 M HNO ₃)
Al	3.1±0,6	< DL	3.7±0.5
V	30±3	30±3	< DL
Fe	15±3	< DL	16±3
Ni	32±5	33±5	0.6±0.2
Zn	1.8±0.3	< DL	1.6±0.5

¹ direct input of HOR solution in toluene to ICP-AES spectrometer

4. CONCLUSIONS

Virtually all heavy oil enriched by V, Ni, Re, Mo, Se, U, Sb, As, Au, Cd, and other rare trace elements whose contents can reach the level of concentration in metal ores used industrially. Important advantages of the extraction methods of extraction are universal with respect to the nature of the selectable items and their concentration, ease and speed of implementation. Furthermore, a method of extraction of metals from the discharge oil feedstock will solve two problems at once - obtaining a concentrate of valuable elements, on the one hand, and purification from catalytic oil feedstock poisons (many metals which are present in the oil), on the other hand. Results obtained could be very useful for unique research in theoretical modeling of Earth's origin and oil genesis.

Extraction with using of nitric acid solution as the main extractant allows to recover most of valuable elements from oil/oil products irrespective of their viscosities almost completely, except V, Cr and Ni. It could be explained by high binding energy of those metals in metalorganic compounds and, as consequence, higher solubility in the oil phase than in the aqueous acid solutions used. Modifiers, namely, organic solvents and complexing reagents can be added to nitric acid solution for the increase of extraction degree of those metals. The development of a method for the extraction pre-concentration of metals to obtain a concentrate of valuable elements from heavy oil and processed products (in particular, the heavy oil residue) allow to use oil as a non-traditional sources of raw materials for the production of metals.

ACKNOWLEDGEMENTS

This work was supported by the Russian Ministry under the Federal Program "Research and development on priority directions of scientific-technological complex of Russia for 2014-2020" (state contract № 14.576.21.0043).

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