THE DEVELOPMENT OF APPROACHES FOR ELEMENTAL ANALYSIS OF THE HEAVY OILS AND OIL RESIDUES

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Abstract

Heavy oil and heavy oil residues often contain a wide range of non-ferrous, rare and noble metals in high concentration. Standard methods of elemental analysis of heavy oil and heavy oil residues does not exist. Two approaches for the oil metalliferous feedstock analysis were proposed. There are direct analysis by ICP-AES and preliminary extraction of metals to the aqueous solution of an inorganic acid, followed by instrumental analysis. The possibility of pre-concentration of metals oil prior to analysis was shown. The developed methods of analysis allows identifying most of the elements in the heavy oil feedstock for a short time with a high degree of reliability.

Key words: *heavy oil residues, heavy oils, elemental analysis, sample preparation, demetallization, concentration*

1. INTRODUCTION

Heavy oil deposits most enriched with various metals (V, Ni, Re, Mo, Se, U, Sb, As, Au, Cd and other rare and trace elements), the contents of which can reach the level of industrial ore concentrations. It is considered that trace elements are mainly associated with asphaltenes and resinous oil components (Kolodyazhni 2006). It is known that asphaltenes and resins are the main components of the heavy oil residue (HOR) formed during refining. So in the process of refining the majority of the metals included in its composition are concentrated in the HOR. Of course, the set of elements found in HOR depends on the elemental composition of the original oil. The concentration of the metal and resinous-asphaltene compounds in heavy oil residues 2 - 4 times higher than in oil. There are mainly nickel and vanadium in heavy oils, which are exist as organometallic compounds and as metalloporfirin complexes (25% of the total content of metals in the residue).

It should be noted the heavy oil residues often accumulate at refineries as waste, although their constituent components (such as metals) may undoubtedly be of interest in the production of high added value products. The main problem is the absence of standard methods of elemental analysis of heavy oil feedstock.

Techniques recommended by the ISO (International Organization for Standardization), UOP (US by Universal Oil Products), ASTM (American Society for Testing and Materials), EN (European Committee for Standardization) are generally used for determination of oil elemental composition during the oil refining processes. Standard methods of elemental analysis of heavy oil and heavy oil residues does not exist.

The aim of this work was to study the possibilities of application of modern sample preparation and analysis methods for the investigation of heavy oil and heavy oil residues elemental composition. The research was carried out in two ways: direct analysis of petroleum feedstock by spectral methods (atomic-emission spectrometry with inductively coupled plasma, ICP-AES) and analysis after sample preparation, including recovery of metals from heavy oil and HOR by flow extraction method.

2. MATERIALS AND METHODS

2.1. Reagents and materials. In all the experiments on the decomposition of samples and for the preparation of solutions, deionized water (resistivity 18.2 MΩ) was applied obtained using a Milli-Q water purification system (Millipore, Canada), and 65% HNO_3 (containing no more than 5 x 10"7% Hg) GR. ISO 1.00452.2500 (Merck, Germany). As diluents of highly viscous samples, we used toluene and o-xylene (cp grade), as they are the best solvents for sample of heavy oil residues.

To construct the calibration curves (in the determination by 1CP-AES), standard solutions were prepared by diluting the Conostan multielement standard (Canada) with a concentration of 900 pg/g of each element (Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn. Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn) in the form cyclo-hexanebutyrates in light oil.

The objects of the study were heavy oil residues of oil from Chernigovskoe deposit with density 1.025 g/cm^3 and viscosity 765.8 mm^2/sec

2.2. Apparatus. To determine trace elements, we used a Thermo Scientific iCAP 6500 Duo inductively coupled plasma atomic emission spectrometer with an ISOMIST accessory.

2.2.1. The autoclave decomposition. The autoclave decomposition of the samples of heavy oil residues for the subsequent analysis was carried out using an MKP-04 autoclave module with six autoclaves (ANCON-AT-2, Russia). Samples weighing 0.5 g were heated in sealed Teflon containers (time of sample heating in the autoclave was 4 h (1 h at 160, 1 h at 180, and 2 h at 200°C) with 10 mL of $HN0_3$, then cooled and diluted with deionized water to 50 mL.

2.2.2. Dissolving of heavy oil residues. Samples of heavy oil residues were dissolved in various organic solvents using an SJ45/40 Soxhlet apparatus (dissolution with solvent vapors) 100 mL in volume (S1MAX, Russia) and a shaker (ELMI. Russia). The samples were warmed in an oven at 100°C. A 1-g portion of the sample was transferred into a 100-mL flask; 60 mL of solvent (toluene or o-xylene) was added; the flask was covered with a ground stopper; and the mixture was thoroughly mixed in a shaker for 15 min. In the using of a Soxhlet apparatus, a weighed 1 -g portion was transferred onto paper filter (white ribbon). The paper filter with a sample was shaped into a sleeve and placed in a Soxhlet apparatus. In a 250-mL round bottom flask with ground joint 60 mL of solvent (toluene or o-xylene) was placed using a measuring cylinder. A reflux condenser and a round bottom flask were connected to the Soxhlet device. The sample was dissolved with solvent vapors in the Soxhlet apparatus for 90 min. The completeness of the experiment was controlled by a complete bleaching of the solution in the extraction chamber of the Soxhlet apparatus. After dissolving the sample with solvent vapor, the mixture was poured into a 100-mL flask and closed with a ground glass stopper.

In order to avoid distortion of the results, a blank experiment was carried out, consisting in the extraction of elements from the paper filter (white ribbon) without sample under the same conditions. The obtained values were taken into account in the processing of the results.

2.2.3. Extraction pretreatment using rotating coiled column. Rotating coiled column (RCC) is the principal unit of planetary centrifuge (Figure 1) and it is a Teflon tube wound in the form of single or multi-spiral on a rigid or flexible core planetary centrifuge. Scheme of planetary centrifuge is shown in Figure 2.
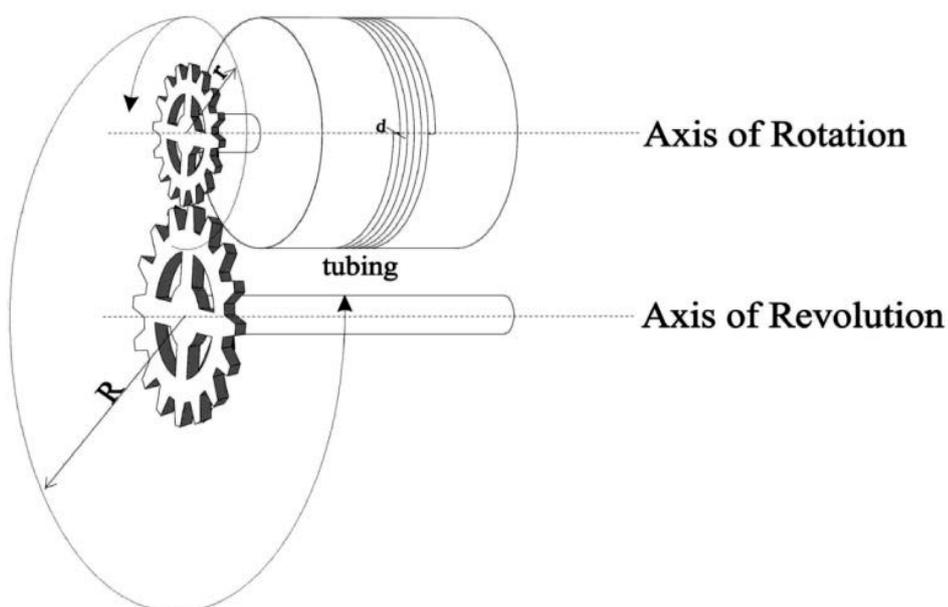
Figure 1. Planetary centrifuge

Figure 2. Scheme of planetary centrifuge, where *r* is spool radius and *R* is rotor radius.

One phase (stationary, the acid solution) is held in the RCC without solid support or sorbent due to influence of the mass forces occurring during rotation of the column about its own axis (axis of rotation) and its simultaneous rotation around the central axis of the device (axis of revolution), while the second phase of the system (mobile, oil) is continuously pumping through the column.

3. RESULTS AND DISCUSSION

3.1. Analysis of petroleum feedstock by direct input into the spectrometer

Atomic emission spectrometry (AES) is the most common express highly sensitive method for

identification and quantification the elements of impurities in gases, liquids and solids, including high-purity ones. Atomic emission spectrometry with inductively coupled plasma (ICP-AES) was developed in the early of 1960-s. The method is based on measurement of the radiation intensity of the light emitted by atoms at specific wavelengths after excitation by inductively coupled argon plasma. It is used to determine the concentrations of the different elements. The detection limits (DL) of ICP-AES are usually very low. The DL are 1-100 g/l for many elements during the continuous introduction of the sample into the plasma. There are many lines of varying intensity for each element in the spectrum, so the inductively coupled plasma (ICP) is suitable for measuring any concentration ranging from ultra- to macroconcentrations. If you use an ICP with a suitable spectrometer, it is possible to simultaneous determination of a large number of elements. Full multivariate analysis can be performed for only 30 seconds at a sample solution flow rate 0.5 ml.

Generally, the samples analyzed by ICP-AES, are aqueous solutions.

In papers published in the early of 70-s of the last century, there is evidence on the analysis of metals in solutions of organic substances by ICP-AES (Gruitt 1970, Miyazaki 1982). The main problem was the instability of the plasma discharge during the introducing to ICP a most of organic solvents (e.g. ethanol, carbon tetrachloride, toluene). So, because of the instrumental complexity researchers refused direct analysis of organic solutions and determine elements in aqueous solutions after mineralization, back-extraction and distillation of the solvent.

Modern instruments for the implementation of ICP-AES method allow varying the operating parameters in a wide range. Spectrometer Thermo Scientific iCAP 6500 Duo with an ISOMIST accessory is one of these devices.

The choice of solvent and optimal operation of the device were selected to develop the method of heavy oils and heavy oil residues analysis by directly entering of the sample solution into the spectrometer. Heavy oil residue was chosen as an object of research because its viscosity higher then oil.

The choosing a solvent for HOR was based on the following requirements to organic solvents: universality, accessibility and low cost, high solubility of HOR. Some solvents (toluene and o-xylene) satisfy these requirements. Hexane and pentane, which are also used for the dissolution, were excluded from the list, because asphaltenes precipitate therein.

The device parameters allowed introducing toluene/o-xylene and, respectively, HOR solutions into the plasma were chosen:

Power delivered to the plasma is 1250 W

The maximum flow rate of argon:

The plasma - 16 l/min.

Subsidiary - 1.0 l/min.

Spraying - 0.15 l/min.

Observation of plasma - axial

It is necessary to prepare a HOR solution in an organic solvent to enter the heavy oil residue into the spectrometer. In the present study two methods for HOR dissolving were examined:

1. dissolving under shaking on a shaker

2. dissolution in a Soxhlet apparatus (dissolution by solvent vapors)

The results of determination of the HOR elemental composition obtained for solutions (prepared in Soxhlet apparatus and using shaker) are shown in Table 1.

Table 1. Results of determination of elements in HOR solutions by ICP-AES, after dissolving by use of the shaker and Soxhlet apparatus

Element	λ, nm	Solution of HOR in toluene		Solution of HOR in o-xylene	
		Soxhlet apparatus	Shaker	Soxhlet apparatus	Shaker
Mg	279,5	0,32±0,07	0,22±0,02	0,18±0,01	0,18±0,01
Al	308,2	3,8±0,9	3,5±0,8	2,7±0,1	3,0±0,2
Ca	317,9	1,0±0,31	0,77±0,17	1,0±0,1	0,88±0,27
V	309,3	89,5±0,8	91,2±4,0	63,6±0,4	66,3±0,4
Ni	221,6	29,9±0,1	27,6±5,5	21,9±0,3	22,3±0,2
Zn	213,8	2,0±0,1	1,7±0,3	1,0±0,1	0,82±0,04
Time for elements recovery, min		90	15	90	15

As seen from the table, the results of the determination of elemental composition of HOR are comparable in both cases. However, the preparation of the solution by use a shaker takes significantly less time than using Soxhlet apparatus (15 and 90 minutes respectively). Therefore, shaker is recommended for solutions preparing. Furthermore, it is possible simultaneously dissolve few HOR samples using shaker. The method developed allows determining most of the elements in the HOR for a short time and can also be used for the elemental analysis of the heavy oil and oil fractions.

3.2. Analysis of petroleum feedstock for pre-extraction of metals

The multi-stage extraction was used for sample preparation of heavy oil and heavy oil residue without thermal decomposition before the elemental analysis.

It has previously been shown (Soin 2010), that the extraction method of sample preparation that is based on the use of planetary centrifuge (figure 1) allows preconcentrating trace elements from crude oil prior to their determination by instrumental methods (e.g. atomic emission spectrometry with inductively coupled plasma ICP-AES).

According to previous studies of crude oil samples (Soin 2010), the density and viscosity of testing samples should not exceed 0.85 g/cm^3 and 7 mm^2/s respectively. This is required for efficient extraction of inorganic constituents from the oils and oil residues. Samples with higher density and viscosity should be diluted by mild solvents.

The choosing of a solvent for heavy oils and HOR was based on the following requirements to organic solvents: universality, accessibility and low cost, high solubility of samples. Toluene and o-xylene satisfy these requirements (Musina 2014).

Nitric acid solution (1.0 M) was used as an extractant (stationary phase). The volume of stationary phase was 10 ml.

Table 2 shows the results of trace elements determination in the HOR Chernigovskaya solution in toluene and o-xylene by ICP-AES after prior extraction using RCC.

Table 2. The results of trace elements determination in the HOR Chernigovskaya solution in toluene and o-xylene by ICP-AES after prior extraction using RCC

| Element | Concentration, mg/kg | |
| | HOR solution | |
	toluene	o-xylene
Na	4,1±0,6	4,0±0,6
K	4,3±0,5	4,2±0,6
Al	2,5±0,5	3,0±0,5
Ni	0,41±0,08	0,35±0,11
Ca	1,7±0,2	1,6±0,2
Mg	0,41±0,12	0,40±0,12
Mn	0,39±0,11	0,35±0,11
Fe	18,9±3,4	16,8±3,1
Cu	0,47±0,12	0,78±0,12
Zn	1,8±0,2	1,5±0,2
Sr	1,1±0,2	0,97±0,2
Cd	< DL	< DL
Ba	0,37±0,11	0,32±011
Pb	< DL	< DL
Cr	0,76±0,12	0,67±0,12
V	< DL	< DL

As can be seen from Table 2, the results obtained using toluene and o-xylene as a solvent of HOR are practically comparable. In further studies toluene was used as the solvent of HOR. Vanadium content in the sample is below the detection limit (software) probably due to the fact that most often vanadium is found in oils in the form of strong porphyrin complexes. Destruction of them under the our experimental conditions is impossible.

Validation of the results was performed by addition method using the standard solution Konostan S-21. Additives of defined elements were introduced in HOR solutions, and then carried out the extraction to 1.0 M nitric acid solution using RCC. The initial concentration of elements in the HOR solution was also determined using multi-step extraction pretreatment procedure in RCC under the same experimental conditions. Table 3 shows the validation results of the elemental analysis of the HOR Chernigov solutions by ICP-AES.

Table 3. Validation results of the of the elemental analysis of the HOR Chernigov solutions by ICP-AES (n = 3, P = 0,95)

Element	Concentration, µg/mL			
	Initial (preliminary determined)	Added	Total (calculated)	Measured
Ca	0,03	0,25	0,28	0,29±0,02
		1,20	1,23	1,33±0,2
		3,50	3,53	3,33±0,4
Fe	0,32	0,25	0,57	0,55±0,02
		1,20	1,52	1,62±0,2
		3,50	3,82	3,92±0,4
Al	0,04	0,25	0,29	0,28±0,02
		1,20	1,24	1,24±0,2
		3,50	3,54	3,54±0,4
Cr	0,01	0,25	0,26	0,26±0,02
		1,20	1,21	1,21±0,2
		3,50	3,51	3,61±0,4
Zn	0,03	0,25	0,28	0,27±0,02
		1,20	1,23	1,24±0,2
		3,50	3,53	3,23±0,4

Table 3 shows that the measured concentrations of trace elements in HOR solution are agree with the total calculated concentration of elements.

4. CONCLUSION

Two approaches for the oil metalliferous feedstock analysis were proposed. There are direct analysis by ICP-AES and preliminary extraction of metals to the aqueous solution of an inorganic acid, followed by instrumental analysis. The extraction of metals to the mineral acid solution allows recovering most of elements from oil sample and allows pre-concentrating metals in aqueous solution. Consequently, it is possible to detect the elements contained in the crude oil in low concentrations, and inaccessible to the determination by other sample preparation methods. The developed methods of analysis allows identifying most of the elements in the heavy oil feedstock for a short time with a high degree of reliability

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