

## Research Article

# New Possibility for REE Determination in Oil

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A novel approach of rare earth elements (REE) determination in crude oil is suggested. Special application of countercurrent chromatography (CCC) is used as a sample pretreatment tool. An oil sample is continuously pumped through the rotating coil column (RCC) as a mobile phase, while an aqueous phase (nitric acid solution) is retained as a stationary phase. Two phases are kept well mixed and agitated, but there is no emulsion at the interface under the chosen conditions. Special features of CCC give an opportunity to vary the volume of oil samples to be analyzed from 10 mL to 1 L or more. Trace metals are preconcentrated into 10 mL of stationary phase (acidic solutions) pumped out of the column so that analysis can be easily determined with inductively coupled plasma mass spectrometry (ICP-MS) without additional sample preparation procedures. Optimal concentration of nitric acid in the stationary phase for preconcentration of REE from oil by CCC has been investigated. The combination of CCC with ICP-MS gives the possibility to develop a rapid, reliable, and accurate method of trace metal including rare earth elements (REE) determination in crude oils and oil products. Such method could be an alternative for unexpanded and expensive neutron-activation analysis (NAA).

## 1. Introduction

Microelemental and REE contents of oil are very important for estimating oil's age and for developing theories of oil's origin. It is known that information about hydrocarbons genesis could be obtained using element ratios. Such ratios also could be determinative as the georeconnaissance data. From this point of view, REE content/ratios are of the prime interest. REE ratios could be used as the reference points for different oils (from different deposits/fields) like for most geological samples as rocks, minerals, and ores [1, 2].

In the meantime, REE analysis of oils is still a very complicated analytical task. There are no methods of preconcentration of metals from oil to aqueous phases, and REE contents are usually at ppt level and lower. Also there are no standard methods (ASTM D, IP, EN, or UOP) or standard/reference samples for REE analysis of oils. It should be mentioned that articles and studies dedicated to REE content in oils could be found really seldom. Thus, ICP-MS determination of REE in oils was published [3] when acid digestion was used for sample preparation. As a result, most

of REE, measured (including Pr, Sm, Eu, Gd, Dy, Er and Yb) were "not detected."

Suggesting hybrid method (CCC and ICP-MS) enables lessening detection limit (DL) and detecting most of metals in oil including REE.

Abilities of the liquid stationary phase retention during pumping of oil samples through column enable isolation and preconcentration of the inorganic impurities into acidic aqueous solutions. In this case, CCC can be used as a tool for the sample pretreatment and preparation. Preliminary investigations on retention features of oil/oil products—aqueous phase systems in CCC, were published [4, 5].

The main characteristic of sample preparation methods is recovery values. It is preferable to compare recoveries of inorganic impurities from oil by extraction method and other instrumentation techniques. If that instrumentation method enables direct oil analysis, then comparison will be more reliable. Thus, NAA was used in this work. Aforesaid issue of standard/reference samples is a real problem for extraction/leaching methods as well. Therefore, relative contents of REE were mainly used.

Thus, regardless of the geological and tectonic structure of the source regions, oil composition, depth of deposit occurrence, and lithology of the enclosing rocks, the distribution curves of REE are usually highly differentiated. It has been shown also that total quantity of lanthanides ( $\Sigma \text{Ln}_N$ ) has a very wide range from 0.5 to 5.8 mg/t (3.0 mg/t on average) in West Siberian and Kazakhstani oils. As an example, fluids of cooling magma pockets of increased alkalinity are the major source of lanthanides in oil. They are involved in oil enrichment with light lanthanides and formation of the positive Eu anomaly [6].

Main objective of this work was to estimate CCC-ICP-MS approach to REE determination of oils from different sources and to compare with the results obtained by NAA.

## 2. Experimental

**2.1. Reagents and Materials.** High-purity deionized water (resistivity 18.2 m $\Omega$ ) obtained from a Milli-Q water purification system (Millipore, Canada) and ultrapure nitric acid HNO<sub>3</sub> (Merck, Germany) for aqueous solution preparing and decomposition of oil samples and as a stationary phase has been used.

In the quantitative elemental analysis by ICP-MC, we prepared standard solutions by diluting multielement agilent standard 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, and Zn 10  $\mu\text{g}/\text{mL} \pm 0.5\%$  in 2% HNO<sub>3</sub>). Elements concentration range for all the elements was 1–100  $\mu\text{g}/\text{L}$ .

Calibration coefficients of determination for all elements were 0.9995–0.9999. Recovery tests were performed using “Trace metals in drinking water” solution (with 2–250  $\mu\text{g}/\text{L}$  concentrations of Al, As, Ba, Be, Bi, Cd, Cr, Co, Cu, Fe, Pb, Li, Mn, Mo, Ni, Rb, Sb, Se, Sr, Te, Tl, U, V, Zn, and Ag), and recoveries were in the range of 91–112%.

Experiments on trace and rare earth elements preconcentration were performed with light Kazakhstan (Tengizskaya) oil with density  $\rho = 0.795 \text{ g}/\text{mL}$  and viscosity  $\eta = 2.270 \text{ mm}^2/\text{s}$ , West Siberian oil (region) with  $\rho = 0.870 \text{ g}/\text{mL}$  and  $\eta = 17.90 \text{ mm}^2/\text{s}$  and composite oil with  $\rho = 0.828 \text{ g}/\text{mL}$  and  $\eta = 4.745 \text{ mm}^2/\text{s}$ . Tengizskaya oil is a medium-sulfur oil (S content  $\sim 0.9 \text{ mass.}\%$ ), West Siberian oil is a middle-sulfur oil (S content  $\sim 1.6 \text{ mass.}\%$ ), and composite oil is a medium-sulfur oil (S content  $\sim 0.8 \text{ mass.}\%$ ).

### 2.2. Instruments

**2.2.1. RCC.** Figure 1 schematically illustrates type J single-layer synchronous planetary centrifuge. Typical column is formed by winding Teflon tubing around a cylindrical holder. Column holder rotates around its own axis and revolves around the centrifuge axis at the same speed ( $\omega$ ) and in the same direction. 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-3 M” J-type single-layer synchronous horizontal planetary centrifuge (made in the Institute for Analytical Instrumentation,

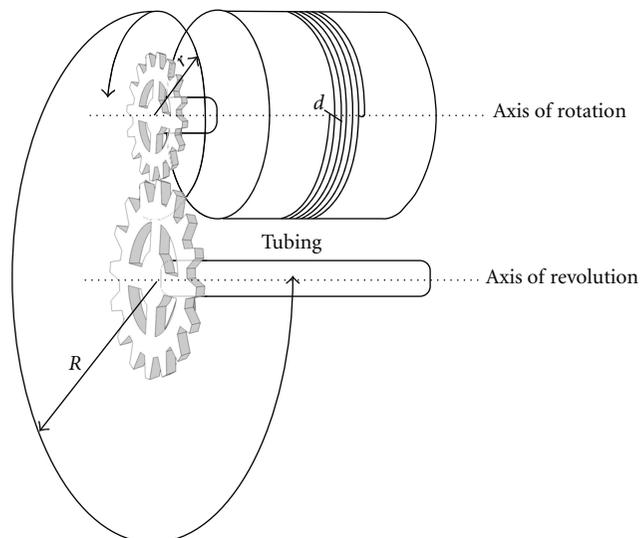


FIGURE 1: Scheme of planetary centrifuge.

St. Petersburg, Russia) with the total column volume of 19 mL at constant  $T = 20^\circ\text{C}$ . Scheme of planetary centrifuge is in Figure 1. RCC coiling diameter was 120 mm, revolution radius was 93 mm, and length of the tube was 1.15 m. Phases were pumped through an RCC using a peristaltic pump (Masterflex, UK).

The column was filled with aqueous HNO<sub>3</sub> solution while stationary. Then the planetary centrifuge is set to rotate at constant speed, and the mobile phase (oil or diesel) was pumped through the column from the top of the column to the bottom or “Head to Tail” [4, 5, 7]. Some volume of the aqueous acid solution is retained in the column as the stationary phase. All working parameters for the planetary centrifuge are shown in Table 1. 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 CCC experiment, 70–100 of each solvent were pumped through the stationary column.

**2.2.2. Autoclave Decomposition.** To compare results of CCC 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. Standard conditions of autoclave decomposition are provided in Table 2. Oil samples were digested by concentrated ultrapure HNO<sub>3</sub> in sealed Teflon containers and then 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.

**2.2.3. ICP-MS Determination.** ICP-MS measures most of the elements with very low (ppb or even ppt) DLs. Minimization of large interferences was provided with a simple matrix of analyzed samples (diluted HNO<sub>3</sub> solutions), maximal comp-

TABLE 1: Working parameters of planetary centrifuge.

Mobile-phase volume	Stationary-phase volume	Centrifuge rotation speed	Beta ratio (spool radius/rotor radius)	Flow rate of mobile phase	Column tubing bore	Temperature
$V_M$ , mL	$V_S$ , mL	$\omega$ , rpm	$\beta = r/R$	$F$ , mL/min	$d$ , mm	$T$ , °C
19–110	10	750	0.65	0.5; 1.2	0.8	20

TABLE 2: Conditions and working parameters of autoclaves decomposition of oil sample.

Sample mass	Acid volume	Time and temperature		
		1	2	3
$m_s$ , g	$V_{\text{HNO}_3}$ , mL	1 h—160°C	1 h—180°C	2 h—200°C
0.5	10			

TABLE 3: Instrumental parameters for determination of metals by ICP-MS.

Forwarded power	1200 W
Analog stage voltage	−1800 V
Pulse stage voltage	1100 V
Argon consumption	
Plasma generating flow	15 L/min
Auxiliary flow	0.8 L/min
Carrier flow	1.4 L/min
Sample consumption	0.5 mL/min
Peak resolution	~0.6 amu
Detector operating modes	Pulse count and analog
Speed of peristaltic pump	24 rpm
Spray chamber	Cooling (4°C) quartz
Mass range	27–238 amu
Sweeps/reading	40
Replicates	3
Dwell time	50 ms
Scan mode	Peak hopping
Abundance sensitivity	
Low mass	$<5 \cdot 10^{-7}$
High mass	$<1 \cdot 10^{-7}$

liance with the standards matrix, and optimization of the instrument parameters.

Performance of the ICP-MS instrument strongly depends on the operating conditions. Tuning solution containing Li, Y, Ce, Tl, Co (10  $\mu\text{g/L}$ ) in 2 wt% aqueous  $\text{HNO}_3$  was used to optimize the instrument (Agilent 7500c, USA) in terms of sensitivity, resolution, and mass calibration.  $^{140}\text{Ce}^{16}\text{O}^+ / ^{140}\text{Ce}^+$  and  $^{137}\text{Ba}^{2+} / ^{137}\text{Ba}^+$  ratios were used to minimize oxide ions and double-charged ions levels in the plasma that could interfere with the determination of some elements.

Measurement parameters such as carrier gas flow, torch position, speed of peristaltic pump, and dwell time were optimized with the aim of high sensitivity and low isobaric interferences. ICP-MS analysis was performed following the operating program and parameters shown in Table 3.

All ICP-MS data (final concentrations in analyzed solutions, calibrations, tunes, statistics, etc.) were obtained from ICP-MS Top Agilent program pack.

Final REE concentrations ( $C$ ,  $\mu\text{g/g}$ ) in oils were calculated using the following standard formula:

$$C = \frac{(A_{\text{sample}} - \bar{A}_{\text{blanks}}) \cdot V}{m}, \quad (1)$$

where  $A_{\text{sample}}$  is the concentration of each element in sample solution ( $\mu\text{g/L}$ ) obtained from ICP-MS (counted by ICP-MS Top Agilent software),  $A_{\text{blanks}}$  is the mean concentration of each element in blank solutions (nitric acid was pumped through the column in 3–5 repetitions),  $V$  is the volume of oil (mobile phase) pumped through the column in CCC experiments, and  $m$  is the mass of analyzed oil.

2.2.4. NAA. Measurements were conducted at Central Laboratory of Substance Analysis of Vernadsky Institute of Geochemistry and Analytical Chemistry RAS. Analyzed oil samples of 10–50 mg were placed in a bag of aluminum foil  $10 \times 10$  mm in size together with certified reference materials (ST-1A, effusive basalt; SGD-1A, intrusive basic rock; AN-G, intrusive basic rock). The bag is placed in an aluminum case and irradiated with a neutron flux of  $1.2 \times 10^{13}$  neutron  $\text{cm}^{-2} \text{s}^{-1}$  for 15 h. The samples are cooled for 6 days to reduce activity of radionuclides with  $T_{1/2} < 15$  h. Then gamma spectra of samples are measured using a Ge or a Ge(Li) detector with a multichannel pulse analyzer for activity levels of 100 and 2000 s, respectively. Measurements are repeated after 6 to 10 days to distinguish gamma lines of relatively long-lived radionuclides. The gamma spectra obtained are processed using the program package described in [8, 9] and by comparing the normalized peak areas of the studied and reference samples. Element concentrations are calculated with regard to their concentrations in the reference samples.

2.3. Results and Discussion. Application of CCC for REE recovery was tested on Tengizskaya oil. Table 4 provides measured concentrations of 12 REE from Tengizskaya oil. Various volumes of analyzed oil (52, 104, and 624 mL) were pumped at the constant flow rate of 1.2 mL/min through the CCC column rotating at 750 rpm. Minimal  $\text{HNO}_3$  concentration (0.5 M) was used for all CCC experiments because of no emulsion at the oil-water interface [10]. Nitric acid with higher concentrations can form some emulsion on the oil-water interface and that means bleed of the stationary phase. It is obvious that concentration factor (5, 10, and 60, resp.) did not affect obtained REE concentrations. The choice of the concentration factor is upon sample quantity and sample preparation time. It is also clearly seen that concentrations

TABLE 4: Measured REE concentration in Tengizskaya oil by ICP-MS after CCC preconcentration from different sample volumes of Tengizskaya oil.

Element	Concentration, $\mu\text{g}/\text{kg}$		
	$V_M = 52 \text{ mL}$	$V_M = 104 \text{ mL}$	$V_M = 624 \text{ mL}$
Y	$0.019 \pm 0.004$	$0.021 \pm 0.004$	$0.023 \pm 0.004$
La	$0.133 \pm 0.02$	$0.075 \pm 0.02$	$0.091 \pm 0.02$
Ce	$0.06 \pm 0.01$	$0.06 \pm 0.01$	$0.05 \pm 0.01$
Pr	$0.006 \pm 0.001$	$0.006 \pm 0.001$	$0.007 \pm 0.001$
Nd	<0.001	<0.001	<0.001
Sm	$0.006 \pm 0.001$	$0.004 \pm 0.001$	$0.005 \pm 0.001$
Eu	$0.018 \pm 0.004$	$0.021 \pm 0.004$	$0.017 \pm 0.004$
Gd	$0.011 \pm 0.003$	$0.014 \pm 0.003$	$0.013 \pm 0.003$
Tb	$0.0020 \pm 4E - 4$	$0.0020 \pm 4E - 4$	$0.0020 \pm 4E - 4$
Dy	$0.0030 \pm 6E - 4$	$0.0030 \pm 6E - 4$	$0.0030 \pm 4E - 4$
Ho	$0.0010 \pm 2E - 4$	$0.0010 \pm 2E - 4$	$0.0010 \pm 4E - 4$
Er	$0.0020 \pm 4E - 4$	$0.0020 \pm 4E - 4$	$0.0030 \pm 4E - 4$
Yb	$0.005 \pm 0.001$	$0.005 \pm 0.001$	$0.005 \pm 0.001$
Lu	<0.0005	<0.0005	<0.0005

TABLE 5: Measured REE concentration in Tengizskaya, West Siberian, and composite oils by ICP-MS after CCC preconcentration.

Element	Concentration in oils, $\mu\text{g}/\text{kg}$		
	Tengizskaya	West Siberian	Composite
Y	$0.019 \pm 0.004$	$0.007 \pm 0.001$	$0.012 \pm 0.002$
La	$0.133 \pm 0.023$	$0.208 \pm 0.036$	$0.037 \pm 0.004$
Ce	$0.06 \pm 0.01$	$0.012 \pm 0.002$	$0.0040 \pm 8E - 4$
Pr	$0.006 \pm 0.001$	$0.0020 \pm 4E - 4$	$0.0020 \pm 4E - 4$
Nd	<0.001	$0.007 \pm 0.002$	$0.0030 \pm 6E - 4$
Sm	$0.006 \pm 0.001$	$0.0020 \pm 4E - 4$	$0.0020 \pm 4E - 4$
Eu	$0.018 \pm 0.004$	$0.0020 \pm 4E - 4$	$0.0004 \pm 1E - 4$
Gd	$0.011 \pm 0.003$	<0.0002	$0.0004 \pm 1E - 4$
Tb	$0.0020 \pm 4E - 4$	$0.0030 \pm 6E - 4$	$0.0002 \pm 5E - 5$
Dy	$0.0030 \pm 6E - 4$	$0.0010 \pm 2E - 4$	$0.0005 \pm 1E - 4$
Ho	$0.0010 \pm 2E - 4$	$0.0010 \pm 2E - 4$	$0.0003 \pm 1E - 5$
Er	$0.0020 \pm 4E - 4$	$0.0010 \pm 2E - 4$	$0.0002 \pm 1E - 5$
Yb	$0.005 \pm 0.001$	$0.0010 \pm 2E - 4$	$0.0005 \pm 1E - 4$
Lu	<0.0005	<0.0005	<0.0005

of REE are very low with  $\Sigma\text{Ln}_N \sim 0.2 \text{ mg}/\text{t}$ . In case of low concentration of REE in oil, the highest concentration factor (60 or even higher) should be used especially with the other instrumentation techniques (ICP-AES, AAS).

It should be noted that concentrations of REE in oils are at very low level that cause difficulties of their direct detection.

There are comparative data of REE determination in 3 different oils: Tengizskaya, West Siberian, and composite in Table 5. REE distributions and ratios are given in Figure 2 and Table 6, respectively. For both oils,  $\Sigma\text{Ln}_N$  was about  $0.2 \text{ mg}/\text{t}$ , while composite oil was diluted by lighter kerosene fraction ( $\Sigma\text{Ln}_N \sim 0.1 \text{ mg}/\text{t}$ ). It is also clear that REE ratios are differentiated.

REE contents and ratios of oils from 3 source regions are different (Figure 2, Table 6). Such REE ratios are usually used as geochemical certificates for oils. In the meantime, we obtained "less DL" results for REE in all oils after autoclaves decomposition. DLs were in the range of  $0.3\text{--}0.04 \mu\text{g}/\text{kg}$  and it was impossible to compare results of the two sample preparation techniques.

Therefore, NAA was used in this work as an instrumentation method that enables direct oil analysis (REE detection in the native forms). Only comparison with NAA could be applied as correctness criteria for combined CCC-ICP-MS method. Comparative REE ratios obtained via NNA and CCC-ICP-MS are presented in Table 7. These results prove correctness of both the methods of REE ratios

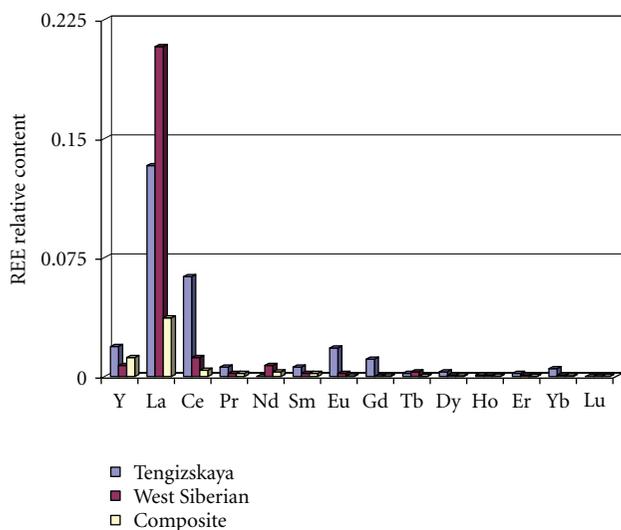


FIGURE 2: Relative REE distributions in Tengizskaya, West Siberian, and composite oil samples.

TABLE 6: Comparative REE ratios of Tengizskaya, West Siberian, and composite oils obtained by ICP-MS after CCC preconcentration.

Oil	Elements ratios			
	La/Ce	Nd/Sm	Eu/Gd	Dy/Ho
Tengizskaya	<b>2.1</b>	—	<b>1.8</b>	<b>3.0</b>
West Siberian	<b>17</b>	<b>3.5</b>	—	<b>1.0</b>
composite	<b>9.3</b>	<b>1.5</b>	<b>1.0</b>	<b>1.7</b>

TABLE 7: Comparative REE ratios of Tengizskaya oil obtained by ICP-MS after CCC preconcentration and by NAA.

Method	Elements ratios			
	La/Ce	Nd/Sm	Eu/Gd	Dy/Ho
NAA	<b>1.8</b>	<b>4.2</b>	<b>1.6</b>	<b>3.0</b>
ICP-MS	<b>2.1</b>	—	<b>1.8</b>	<b>3.0</b>

determination. Both results are not distorted, that is, very important for studying base geochemical processes of the oil genesis.

### 3. Conclusions

It has been shown that REE contents and ratios of oils from 3 source regions are different. Concentrations of REE are very low with  $\Sigma Ln_N \sim 0.2$  mg/t in 3 oil samples studied. Composite oil has  $\Sigma Ln_N \sim 0.1$  mg/t as diluted one with light fraction. Such ratios are usually used as geochemical certificates for oils. Comparative REE ratios obtained via NNA and suggested combined CCC-ICP-MS method are in close agreement. Correct REE ratios could be used for geochemical studies dedicated to oil genesis research.

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