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# Determination of Trace Elements in the Tamsagbulag and Tagaan Els Crude Oils and Their Distillation Fractions Using by ICP-OES

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## ABSTRACT

Thirty one trace elements were determined in the petroleum and its fractions of 200˚C - 350˚C, 350˚C - 450˚C and up 450˚C by inductively coupled plasma optical emission spectrometry. Such analyses are important for technical diagnostics as well as specific sample characteristics. The sample preparation together with an efficient sample introduction allowed a fast quantification of the analytes using calibration curves prepared with analyte organic standards. Trace element occurrences, forms, distributions are examined as well as their implications in terms of reservoir geochemistry, oil refining and environment.

**Keywords:** Trace Elements; Petroleum; ICP-EOS; Fractionation; Tertiary Period; Mesozoi

## 1. Introduction

Crude oil represents a complex mixture containing both organic and inorganic chemical species, being trace metals one group the inorganic components present in this type of matrix [1-3]. Information on trace element concentrations in crude oil is getting increasingly important for the geochemical characterization of source rocks and basins and also to allow corrective actions during crude oil processing [4]. Trace metals have been found in different proportions in different crudes and consequently in their derivatives. Frequently Ni and V are found in largest concentrations contributing to environmental pollution [5-7]. Because of their mutagenic and carcinogenic potential Ni and V emissions have been strictly controlled in several countries. In addition, V is a catalyst poison and causes corrosion in furnaces and boilers during oil processing. The knowledge of the concentration ratio between V and Ni in crude oil provides powerful geological information allowing oil-oil and oil-rock correlation and evaluation of the palaeoenvironmental conditions [8] of sedimentation. Other metals, such as Fe, Cu and Zn, may also be present in significant amounts. Chemical species of these metals can be partially transferred to fractions (fuels for instance), decreasing their quality and performance.

## 2. Experimental

### 2.1. Instrumentation

A Perkin Elmer model Optima 2000 DV Plasma inductively coupled plasma optical emission spectrometer (axial viewing) was used for this study. The instrument is equipped with a dual echelle monochromator, a RF generator of 40 MHz, GemCon nebulizer. A peristaltic pump was used to feed the nebulization system with sample solution. An auxiliary gas flow regulator was used to control the flow of $O_2$ into the nebulizer gas. The operating conditions are listed in **Table 1** [9].

### 2.2. Reagents and Solutions

All reagents employed were of analytical grade. The kerosene was used as solvent in the test as it provides better detection limits and physical property than others [10,11]. ICP Solvent was from Conostan (Ponca City, OK, USA). A multielement organometallic standard (Custom blend, Conoco, Ponca City, OK, USA) with analyte concentration of 500 $\mu g \cdot g^{-1}$ was used to spike the crude oil samples. Two basin (crude oil of XIX-213, 21, 34, 40, 25-50, B 27-42 oil well Tamsagbulag basin and TE 27-5, TE 14-19 oil well Tsagaan els basin.) crude oil samples were used. These crude oil samples were spiked

 

**Table 1. Operating parameters for ICP OES measurements.**

| Parameters | Setting |
|---|---|
| RF power (W) | 1500 |
| Outer argon gas flow rate (L/min$^{-1}$) | 16 |
| Nebulizer gas flow rate: Ar (L/min$^{-1}$)/$O_2$ (L/min$^{-1}$) | 0.6 |
| Intermediate Argon gas flow rate (L/min$^{-1}$) | 0.7 |
| Sample uptake (mL/min$^{-1}$) | 0.8 |
| Position | –3 |

with the multielement organometallic analyte standard (Conostan Custom blend).

## 2.3. Preparation of Samples and Standard

After petroleum samples were dewatered by calcium chloride [12], the water is decreased below 0.08% by determination of Karlo-Fisher method [13]. After dewatering, the petroleum samples were distilled into fractions of diesel (200˚C - 350˚C), oil (350˚C - 450˚C) and heavy residue (above 450˚C) [14].

For preparation of sample, crude oil and its fractions of 200˚C - 350˚C and 350˚C - 450˚C were diluted tenfold, above 450˚C fraction was diluted thirtyfold with kerosene [10].

Conostan Custom Blend standard was spiked to these solutions. Trace elements are determined in samples by comparison standard.

## 3. Results and Discussion

Results of trace elements in petroleum of Tamsagbulag and Tsagaan els basin are shown in **Tables 2** and **3**.

About 30 elements between 0.01 - 35.6 ppm were determined in petroleum of Tamsagbulag and Tsagaan Els basin. The Li is not detected in petroleum of Tamsagbulag and Tsagaan Els basin. The relatively high Na 20.98 ppm in Tamsagbulag, 35.6 in Tsagaan els basin crude oil is noteworthy. This could be incidental due to the contact of crude oil with salt water [16].

**Table 2** presents rare earth elements of Y, La and Sc that were determined 0.01 - 0.07 ppm in petroleum of Tamsagbulag and Tsagaan Els basin. Therefore, it is impossible to use raw material of rare earth elements [3]. Sum trace elements relatively for petroleum of Tamsagbulag and Tsagaan Els, sum trace elements in petroleum of Tamsagbulag more 1.5 than petroleum of Tsagaan Els.

**Table 2** shows that alkali and alkaline earth metals are most of all other group elements. It is alkali metals and alkaline earth metals that are related to earth. Elements of Sub-Group IIIa (Sc, Y, La) are the least of all other group elements.

The content of determined elements is possibly stationing for following decreasing states:

**Table 2. Concentration of trace elements in petroleum, ppm.**

| Element | | Tamsagbulag basin (sample of 6) | Tsagaan Els basin (sample of 2) |
|---|---|---|---|
| Alkali metals | Na | 20.98 | 35.6 |
| | Li | <0.01 | <0.01 |
| Total | | **20.98** | **35.6** |
| Alkaline earth metals | Be | 0.05 | <0.01 |
| | Mg | 0.19 | 1.11 |
| | Ca | 1.78 | 2.63 |
| | Ba | <0.05 | 0.19 |
| | Sr | 0.46 | 2.43 |
| Total | | **2.48** | **6.36** |
| Sub-Group Ib | Cu | 0.51 | 0.37 |
| | Ag | 0.03 | 0.04 |
| Total | | **0.54** | **0.41** |
| Sub-Group IIb | Zn | 3.01 | 0.62 |
| | Cd | 1.65 | 0.26 |
| Total | | **4.66** | **0.88** |
| Sub-Group IIIa | Sc | <0.01 | 0.04 |
| | Y | 0.01 | 0.07 |
| | La | 0.01 | <0.01 |
| Total | | **0.02** | **0.11** |
| Sub-Group IIIb | B | 2.88 | 3.18 |
| | Al | 0.36 | 2.11 |
| Total | | **3.24** | **5.29** |
| Sub-Group IVb | Si | 1.35 | 5.76 |
| | Sn | 0.23 | 0.71 |
| | Pb | 0.18 | 1.16 |
| Total | | **1.77** | **7.63** |
| Sub-Group Vb | P | 0.22 | 0.06 |
| | Sb | 0.14 | 0.15 |
| | Bi | 0.20 | 0.01 |
| Total | | **0.56** | **0.22** |
| Sub-Group VIa | Cr | 1.15 | 1.03 |
| | Mo | 0.39 | 0.29 |
| | W | 2.79 | <0.01 |
| Total | | **4.18** | **1.32** |
| Group VIII | Fe | 2.91 | 4.5 |
| | Co | 0.07 | 0.59 |
| | Ni | 3.68 | 2.82 |
| Total | | **6.66** | **7.91** |
| Other group elements | Ti | 0.18 | 0.29 |
| | V | 0.56 | 0.97 |
| | Mn | 0.06 | 0.17 |
| Sum | | **46.12** | **67.43** |

 

**Table 3. V/Ni ratios in the studied crude oil samples.**

| Coefficient | Tamsagbulag basin | Tsagaanels basin |
|---|---|---|
| V/Ni | 0.15 | 0.34 |
| Geological age of rock | Mesozoi, teriaty | |
| Depositional environment of source | Nonmarine | |
| Oil properties | High wax, low sulfur | |
| Maturity | High maturity | Low maturity |

Oil of Tamsagbulag basin: **Na** > **Ni** > **B** > Zn >W > Sb > Cd, > Si > Ca > Cu >Mo > Cr > Fe > V > Sn > Sr > Al > P > Bi > Pb > Ti > Mg > La > Ag > Co > Mn > ***Be*** > ***Ba*** > Y.

Oil of Tsagaan ELs basin: **Na** > Si > **B** > **Ni** > Sb > Sn > Ca > Fe > Sr > Al > Pb > Mg > Cr > Cu > V > Zn > Co > Mo > Ti > Ag > Mn > Y > P > Sc > ***Ba*** > Bi > ***Be***. In the presented elements of Na, Ni, B in petroleum samples with a higher content and elements of Bi, Be in petro-

**Table 4. Determined result of containing trace elements in petroleum fractions of study sample, ppm.**

| Elements | | Tamsagbulag basin | | | Tsagaan ELs basin | | |
|---|---|---|---|---|---|---|---|
| | | 200˚C - 350 ˚C | 350˚C - 450˚C | Up 450˚C | 200˚C - 350˚C | 350˚C - 450˚C | Up 450˚C |
| Alkali metals | Na | - | 2.76 | 26.05 | - | 3.37 | 36.55 |
| | Li | - | - | - | - | - | - |
| **Total** | | - | **2.76** | **26.05** | - | **3.37** | **36.55** |
| Alkaline earth metals | Be | - | - | 0.01 | - | - | 0.01 |
| | Mg | - | 0.02 | 0.36 | - | 0.8 | 1.21 |
| | Ca | - | 0.63 | 4.17 | - | 1.09 | 5.24 |
| | Ba | - | - | 0.1 | - | 0.01 | 0.40 |
| | Sr | - | - | 1.84 | - | 0.46 | 4.51 |
| **Total** | | - | **0.65** | **6.48** | - | **2.36** | **11.37** |
| Sub-Group Ib | Cu | - | 0.03 | 0.81 | - | 0.40 | 4.58 |
| | Ag | - | - | 0.07 | - | - | 0.07 |
| **Total** | | - | **0.03** | **0.88** | - | **0.40** | **4.65** |
| Sub-Group IIb Total | Zn | - | 0.60 | 6.89 | - | 0.11 | 1.24 |
| | Cd | - | 0.24 | 2.46 | - | 0.06 | 0.48 |
| **Total** | | - | **0.84** | **9.35** | - | **0.17** | **1.72** |
| Sub-Group IIIa | Sc | - | - | - | - | 0.01 | 0.08 |
| | Y | - | - | - | - | 0.05 | 0.15 |
| | La | - | - | - | - | - | 0.01 |
| **Total** | | - | - | - | - | **0.06** | **0.24** |
| Sub-Group IIIb | B | 0.52 | 1.14 | 4.64 | 0.39 | 1.16 | 4.62 |
| | Al | - | - | 1.22 | - | - | 4.13 |
| **Total** | | **0.52** | **1.14** | **5.86** | **0.39** | **1.16** | **8.75** |
| Total Sub-Group IVb | Si | 0.40 | 0.92 | 2.27 | 0.50 | 1.99 | 10.52 |
| | Sn | - | - | 0.60 | - | - | 1.46 |
| | Pb | - | - | 0.06 | - | 0.21 | 2.30 |
| **Total** | | **0.40** | **0.92** | **2.93** | **0.50** | **2.20** | **14.28** |
| Total Sub-Group Vb | P | 0.08 | 0.20 | 0.55 | - | - | 0.13 |
| | Sb | 0.03 | 0.04 | 0.28 | 0.03 | 0.05 | 0.27 |
| | Bi | - | - | 0.47 | - | - | 0.03 |
| **Total** | | **0.11** | **0.24** | **1.30** | **0.03** | **0.05** | **0.43** |
| Total Sub-Group VIa | Cr | - | 1.7 | 3.08 | - | 0.93 | 1.57 |
| | Mo | - | 0.79 | 3.12 | - | 0.13 | 0.51 |
| | W | - | - | 1.82 | - | - | - |
| **Total** | | - | **2.49** | **8.02** | - | **1.06** | **2.08** |
| Group VIII | Fe | - | 0.17 | 7.69 | - | 0.43 | 8.98 |
| | Co | - | - | 0.20 | - | - | 1.20 |
| | Ni | - | - | 10.09 | - | - | 5.74 |
| **Total** | | - | **0.17** | **17.98** | - | **0.43** | **15.65** |
| Other group elements | Ti | - | - | 0.35 | - | 0.02 | 0.58 |
| | V | - | - | 1.54 | - | - | 2.04 |
| | Mn | - | - | 0.19 | - | 0.01 | 0.35 |
| **Sum** | | **2.16** | **8.44** | **80.94** | **2.27** | **11.29** | **99.36** |

 

leum samples with lower content.

Some trace elements ratios were constant in petroleum of common source rocks and dependent on the geological age of the rocks and those ratios were used for tracing source effects. [8,15,17,18]. In **Table 3**, V/Ni ratios were calculated using determined result of elements.

In **Table 3**, the petroleum of Tamsagbulag and Tsagaan els contains the rock with the geological age of the tertiary period and mesozoi because the V/Ni ratio is 0.15 - 0.34 [17]. Also oils of Tamsagbulag and Tsagaan Els derived from lacustrine or non-marine source rocks [8].

In **Table 4**, the determined results are presented containing trace elements in petroleum 200˚C - 350˚C, 350˚C - 450˚C, up 450˚C fractions samples by ICP-EOS.

In **Table 4** shows that elements except of sub-group IIIb, IVb, Vb were not detected in petroleum fraction of 200˚C - 350˚C. All elements were detected in petroleum fraction of up 350˚C.

From the **Figure 1** can see that trace elements are discovered in fraction at 200˚C to 450˚C a very little amount. But about 90 - 95 percent of the total trace elements are contained in fraction above 450˚C. Namely, all elements were determined in heavy fraction which was similar to the results in reference [19-23].

## 4. Conclusions

1) Thirty one trace elements were determined in the petroleum and its fractions of 200˚C - 350˚C, 350˚C - 450˚C and up 450˚C by ICP-EOS. The Li is not detected in petroleum of Tamsagbulag and Tsagaan Els basin. Large amounts of Na/20.98 - 35.6 ppm/in petroleum reveal the contact of petroleum with underground water. Rare earth elements of Y, La and Sc were determined at 0.01 - 0.07 ppm in petroleum of Tamsagbulag and Tsagaan els basin. Therefore, it is impossible to use as raw material for rare earth elements.

2) The petroleum of Tamsagbulag and Tsagaan els basin contains rocks with the geological age of tertiary period and mesozoi because of V/Ni ratio which is 0.15 - 0.34. Also oils of Tamsagbulag and Tsagaan Els were derived from lacustrine or non-marine source rocks.

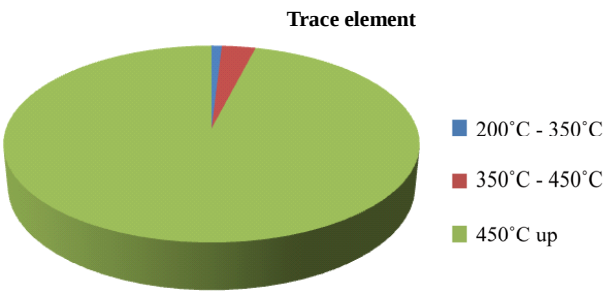


**Figure 1. Trace elements in petroleum fractions.**

3) About 80 - 90 percent of the trace elements are contained in the fraction above 450˚C. Trace elements in petrochemical products are released during combustion, some of them with harmful effects on human health and environment.

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