Determination of Selenium and Nickel in Asphaltite from Milli (Sirnak) Deposit in SE Anatolia of Turkey

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Abstract. Asphaltite is one of the naturally occurring black, solid bitumen’s, which are soluble at heating in carbon disulphide and fuse. Asphaltite is also a solidified hydrocarbon compound derived from petroleum [1]. According to the World Energy Council, Turkish National Committee (1998), the total reserve of the asphaltic substances that are found in south eastern Turkey is about 82 million tons, with Silopi and Sirnak reserves to get her comprising the major part of the Asphaltite deposits. Selenium and Nickel are very important elements both environmental and health. Selenium plays an important role in the formation of the enzyme antioxidant effect in the cell. The need for Selenium increases in situations such as pregnancy, menopause, growth than development, air pollution. Nickel is used for preventing iron-poor blood, increasing iron absorption, and treating weak bones.

In this study, asphaltites were taken from Milli vein from Sirnak deposit in SE Anatolia of Turkey. A total of 6.500.000 tons of Asphaltite reserves have been identified as asphaltites in Milli (Sirnak). The sample preparation method was developed in Asphaltite by spectroanalytical techniques, wet acid digestion. MW-AD followed by ICP-OES were used for the determination of Selenium and Nickel in Asphaltite. Proximate analysis of Asphaltite fly ash samples was made. It also, Selenium and Nickel element analysis in Asphaltite were made.

1. Introduction

Asphaltite is one of the naturally occurring black, solid bitumens, which are soluble at heating in carbon disulphide and fuse. Asphaltite is also a solidified hydrocarbon compound derived from petroleum [1].

According to the World Energy Council, Turkish National Committee (1998), the total reserve of the asphaltic substances that are found in south-easteren Turkey is about 82 million tonnes, with Silopi and Sirkax reserves together comprising the major part of the Asphaltite deposits [2].

Most of the Asphaltite veins in the Sirnak region (Avgamasya, Milli, Seridahli, Nivekara, Karatepe, Ispindoruk, Seguruk) are in form of NE-SW directional fracture fillings in the Germav formation. Milli vein; Asphaltite with large pores and a pyrite content of 4% which is low when compared to other asphaltites. Because it’s max value is 0.38%, its volatile matter is assumed to be high. Clay and similar inorganic matter content reaches 13%. A total of 6.500.000 tons of Asphaltite reserves have been identified as asphaltites in Milli (Sirnak) [3]. It can be seen in Figure 1.
Selenium and Nickel are very important elements both environmental and health. Firstly, Selenium element is named after Selene, the Greek goddess of the moon. The image is of a crescent moon against a cratered surface. Its appearance is a semi-metal that can exist in two forms: as a silvery metal or as a red powder.

The biggest use of selenium is as an additive to glass. Some selenium compounds decolourise glass, while others give a deep red colour. Selenium can also be used to reduce the transmission of sunlight in architectural glass, giving it a bronze tint. Selenium is used to make pigments for ceramics, paint and plastics.

Selenium has both a photovoltaic action (converts light to electricity) and a photoconductive action (electrical resistance decreases with increased illumination). It is therefore useful in photocells, solar cells and photocopiers. It can also convert AC electricity to DC electricity, so is extensively used in rectifiers.

Selenium is toxic to the scalp fungus that causes dandruff so it is used in some anti-dandruff shampoos. Selenium is also used as an additive to make stainless steel. Selenium is an essential trace element for some species, including humans. Our bodies contain about 14 milligrams, and every cell in a human body contains more than a million selenium atoms. Too little selenium can cause health problems, but too much is also dangerous. In excess it is carcinogenic and teratogenic (disturbs the development of an embryo or fetus).

Selenium is found in a few rare minerals. Most of the world’s selenium is obtained from the anode mud product enduring the electrolytic refining of copper. These medusa ree it roasted with sodium carbonate sulphuric acid, or melted with sodium carbonate to release the selenium [4].

Secondly, Nickel element image is of baked beans, which contain a surprising amount of nickel. Its appearance is a silvery metal that resists corrosion even at high temperatures.

Nickel resists corrosion and is used to plate other metal to protect them. It is, however, mainly used in making alloys such as stainless steel. Ni chrome is an alloy of nickel and chromium with small amounts of silicon, manganese and iron. It resists corrosion, even when red hot, so is used in toasters and electric ovens. A copper-nickel alloy is commonly used in desalination plants, which convert seawater into freshwater. Nickel steel is used for armor plating. Other alloys of nickel are used in boat propeller shaft and turbine blades. Nickel is used in batteries, including rechargeable nickel-cadmium batteries and nickel-metal hydride batteries used in hybrid vehicles. Nickel has a long history of being used in coins. The US five-cent piece (known as a ‘nickel’) is 25% nickel and 75% copper.

Finely divided nickel is used as a catalyst for hydrogenating vegetable oils. Adding nickel to glass gives it a green colour.
The biological role of nickel is uncertain. It can affect the growth of plants and has been shown to be essential to some species.

Some nickel compounds can cause cancer if the dust is inhaled, and some people are allergic to contact with the metal. Nickel cannot be avoided completely. We take in nickel compounds with our diet. It is an essential element for some beans, such as the navy bean that is used for baked beans.

The minerals from which most nickel is extracted are iron/nickel sulphides such as pentlandite. It is also found in other minerals, including garnierite. A substantial amount of the nickel on Earth arrived with meteorites. One of these landed in the regions in Ontario, Canada, hundreds of millions of years ago. This region is now responsible for about 15% of the world’s production [5].

In this study, asphaltites were taken from Milli vein from Sırnak deposit in SE Anatolia of Turkey. A total of 6,500,000 tons of asphaltite reserves have been identified as asphaltites in Milli (Sırnak). The sample preparation method was developed in asphaltite by spectroanalytical techniques, wet acid digestion. MW-AD followed by ICP-OES were used for the determination of Selenium and Nickel in asphaltite.

2. Results and discussions
In this study, asphaltites were taken from Milli vein from Sırnak deposit in SE Anatolia of Turkey. The sample preparation method used in this study for determination of Selenium and Nickel amounts in asphaltite by spectroanalytical technique includes wet acid microwave digestion. There have been developed a method of the sample pre-treatment and preparation procedures for Se and Ni determination in Asphaltite. Microwave-acid digestion (MW-AD) followed by ICP-OES we reexamined for determination of Se and Ni in asphaltite.

Asphaltite samples were digested using the Berghof MWS-3 model microwave digestion system. The two-stage five steps microwave acid digestion was applied. 0.5 g dried asphaltite sample was weighed and transferred into a pressure-resistant polytetrafluoroethylene (PTFE) vessel, and the mixture of acids (HNO3+HCl, 3:9 mL) was added. The vessel was then sealed and mounted in a sleeve. It was removed and cooled to room temperature in a water-bath. The method and acid composition of the first step were the same as those for the one-stage digestion except for the digestion program. The vessel was returned to the microwave digestion system and the second stage was applied to the sample under the conditions described in Table 1. The power applied in program was 1250 W. The reaction mixture was subjected to an evaporation module in order to remove the acids after the final digestion. Then the residue was dissolved in Milli-Q water and filtered, and the filtrate was diluted to a fixed volume [6]. The two-stage five steps microwave digestion was carried out as detailed in Table 1.

| Table 1. Operating conditions for two-stage digestion by microwave oven [7] |
|------------------------|--------|--------|--------|------------------------|--------|--------|
| Step 1                 | 1      | 2      | 3      | Step 2                 | 1      | 2      |
| T (°C)                 | 140    | 160    | 190    | T (°C)                 | 160    | 100    |
| Ta [min]a              | 5      | 3      | 5      | Ta [min]a              | 3      | 1      |
| Time [min]b            | 5      | 10     | 20     | Time [min]b            | 15     | 15     |

a Waiting time at desired temperature  
b The time between the two sequential temperatures

After, a Model Optima™ 2100 DV inductively coupled plasma optical emission spectrometer (ICP-OES) (PerkinElmer, Inc., Shelton, CT, USA) was used to determine the different Se and Ni forms.
Spectral wavelengths selection for Se and Ni analysis by ICP-OES are very important; lines chosen should have maximum detection and minimum interference [6]. The Ni: 231.604 and Se: 196.090 nm have been chosen as spectral wavelengths (Table 2).

The limits of detection (LOD) and limits of quantification (LOQ) for Nickel and Selenium metals were determined as follows: 10 free analyses of a blank solution spiked with the metal at a level of very low concentration of the analytical curve were performed. The LOD and LOQ were calculated from the standard deviation (σ) of these determinations (LOD = 3 x σ, LOQ=10 x σ). It can be seen in Table 3 [8].

| Table 2. Operating conditions of the ICP-OES (Perkin Elmer Optima 2100 DV). |
|---------------------------------------------------------------|
| Parameter                     | Value                                |
| RF power (W)                  | 1450                                 |
| Plasma gas flow rate (L min⁻¹) | 15                                   |
| Auxiliary gas flow rate (L min⁻¹) | 0.2                                 |
| Nebulizer gas flow rate (L min⁻¹) | 0.8                                 |
| Sample flow rate (L min⁻¹)    | 1.5                                  |
| View mode                     | Axial                                |
| Read                          | Peak area                            |
| Source equilibration time (s) | 15                                   |
| Read delay (s)                | 50                                   |
| Replicates                    | 3                                    |
| Background correction         | 2-point (manual point correction)    |
| Spray chamber                 | Scott type spray chamber             |
| Nebulizer                     | Cross-Flow GemTip Nebulizer          |
| Detector                      | CCD                                  |
| Purge gas                     | Nitrogen                             |
| Shear gas                     | Air                                  |
| Gas                           | Argon                                |
| Wave length (nm)              | Ni: 231.604, Se: 196.090             |

| Table 3. The analytical performance values for PerkinElmer Optima 2100DV model ICP-OES |
|-----------------------------------------------|
| Element | Linear range (µg kg⁻¹) | Regression | R² | LOD  (µg kg⁻¹) | LOQ  (µg kg⁻¹) |
| Ni      | 0-100                  | y = 43.389 x +10.193 | 0.9954 | 5.49 | 18.28 |
| Se      | 0-100                  | y = 12.364 x + 1.876 | 0.9928 | 10.05 | 33.18 |

Incineration ash (European Commission 0158) Certified Reference Material was used to check the accuracy of the analytical method used (Table 4).

| Table 4. Accuracy assessment through the analysis of the standard reference material constituent elements in Incineration ash (European Commission 0158). |
|-----------------------------------------------|
| Element | Certified (mg kg⁻¹) | Measured (mg kg⁻¹) | Recovery (%) |
| Ni      | 120.6 ± 1.8         | 119.7±0.9          | 99.25        |
| Se      | 10.26 ± 0.17        | 10.43±0.38         | 101.66       |

Finely ground powdered Asphaltite samples (below 0.071 mm), as received, we redried in an oven at 105 °C until a constant weight was reached, and store dover silicagel in a desiccator [1]. Proximate analysis of Asphaltite samples was shown in Table 5.
Table 5. Proximate analysis of Milli, Sirnak Asphaltite

| Moisture (%) | Ash (%) | Volatile matter (%) |
|--------------|---------|---------------------|
| Milli, Sirnak | 0.378   | 51.49               | 14.022               |

The Selenium and Nickel element analysis in asphaltite were made and the results are given in Table 6.

Table 6. The analytical results for determination of Ni and Se in Asphaltite by ICP-OES, (N: 10)

| Ni (mg kg⁻¹) | Se (mg kg⁻¹) |
|--------------|--------------|
| Milli, Sirnak | 3808±9        | 31.90±0.80    |

±Standard Deviation

3. Conclusions

Determination of Ni and Se in Turkish asphaltites was carried out by ICP-OES. The sample preparation method was used for Ni and Se determination in asphaltite by spectro analytical technique. MW-AD followed by ICP-OES was used for the determination of Ni and Se in Asphaltite. Consequently, Milli, Sirnak asphaltite is an economically suitable source of Ni and Se.

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