

DETERMINATION OF VANADIUM IN TURKISH ASPHALTITES

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Vanadium is found in many rocks and minerals, including asphaltite. Asphaltite is one of the naturally occurring black, solid bitumens, which are soluble at heating in carbon disulfide and fuse. Asphaltite is also a solidified hydrocarbon compound derived from petroleum. Determination of vanadium in asphaltite ash was performed by microwave-acid digestion followed by inductively coupled plasma-optical emission spectrometry (ICP-OES) and flame atomic absorption spectrometry (FAAS). Asphaltites from Avgamasya, Harbul, and Segürük deposits in SE Anatolia of Turkey have been investigated. Concentrations of vanadium in Avgamasya, Harbul, Segürük asphaltite bottom ashes were determined using ICP-OES to be 5.871, 4.324, 2.777 g kg⁻¹, respectively.

Introduction

South-Eastern region of Turkey has a relatively large asphaltite potential [1–7]. 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 tonnes, with Silopi and Sirnak reserves together comprising the major part of the asphaltite deposits. Around the region, asphaltite has been the major alternative of lignite for indoor heating, however, asphaltite is not only utilized as a fuel alternative to coal, but used also worldwide as a source of trace metals and for the production of ammonia [8].

Vanadium (V) is one of the most abundant trace elements in petroleum, appearing mostly in organometallic compounds (porphyrines) in concentration levels up to 1000 mg kg⁻¹ and mainly present in the asphaltene fraction [9, 10].

There is a need for the quantification of V in crude oil and its derivatives since it is a serious catalyst poison. V compounds also cause corrosion

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problems, *e.g.* in combustion chambers of power plants [11, 12], V contributes also to environmental pollution, and V emissions are under strict control in several countries because of their potential mutagenic and carcinogenic effects [13]. V in trace amounts (at the $\mu\text{g L}^{-1}$ level) is essential for normal cell growth, but it can be toxic when present in higher (mg L^{-1}) concentrations. Burning of fossil fuels releases V into the air, from where it settles on the soil. Unlike organic pollutants, V is not biodegradable and it may collect in certain ecosystems to the level which may be toxic to living organisms [13]. The accumulation of V in soil reduces the amount of phosphate that plays a very important physiological role in plants [14].

The principal sample preparation methods used for V determination in petroleum and petroleum products by spectroanalytical techniques, besides direct analysis, are dilution with organic solvents, dilution in three-component systems (emulsion or micro-emulsion), dry ashing and wet acid digestion. Direct analysis using little or no sample preparation is most suitable for electrothermal atomic absorption spectroscopy (ETAAS) with a graphite tube furnace and X-ray fluorescence (XRF) [15, 16]. The oil sample might be modified by formation of an emulsion or micro-emulsion (three-component system). Whenever two immiscible liquids are stirred, a macro-emulsion is obtained, either oil-in-water (O/W, droplets of oil in water) or water-in-oil (W/O, droplets of water in oil), depending on the dispersed phase. The kind of emulsion that is formed is mainly related to the formulation and to a lesser degree to the W/O ratio. The use of so-called co-solvent allows the formation of a homogeneous system containing both the aqueous and the organic phases, resulting in a homogeneous and long-term stable three-component solution [17]. Micro-emulsions are formed by a mixture of water, oil and an organic co-solvent, such as a short-chain alcohol (*i.e.* propan-1-ol), because of its molecules [18, 19].

Dry ashing is used for the almost complete elimination of organic materials prior to analyte determination. The time required for this procedure is one of the disadvantages of this method. Another one is the risk of losses of volatile elements or their compounds. As for wet digestion, oxidizing agents are used to decompose organic constituents prior to determination of analyte and boiling points. It can be performed in closed or open vessels, using thermal energy or microwave radiation [20]. Compared to other methods, microwave digestion provides a rapid and efficient method, and it also possesses an advantage of reducing volatilization loss and contamination [21]. A variety of atomic spectrometric techniques has been used for determination of V, among which are atomic absorption spectrometry (AAS) with flame or graphite tube atomizers, inductively coupled plasma optical emission spectrometry (ICP-OES) and XRF [22, 23]. The use of atomic spectroscopic techniques for metal determination in crude oil has been recently reviewed by Hardaway et al. [15].

Experimental

Sample preparation

The sample preparation method used in this study for determination of V in asphaltite by spectroanalytical technique includes dry ashing and wet acid microwave digestion. A method of the sample pretreatment and preparation procedures for V determination in asphaltite bottom ash has been developed. Microwave-acid digestion (MW-AD) followed by ICP-OES and FAAS were examined for determination of V in asphaltite bottom ash (ABA).

Asphaltites were taken from Avgamasya and Segürük veins from Sirnak and Harbul vein from Silopi. Finely ground powdered asphaltite samples (below 0.071 mm), and the certified reference standard materials, as received, were dried in an oven at 105 °C until a constant weight was reached, and stored over silicagel in a desiccator. Proximate analysis of asphaltites was performed according to ASTM procedures. Elemental analysis (C, H, N) of asphaltite samples was made by a Carlo Erba elemental analyzer EA 1108 (Table 1). The dried samples were crushed by means of a jaw crusher type Retsch BB 1/A and ground in a rotor beater mill type Retsch SR2 [1–6]. Samples were accurately weighed in a porcelain crucible and subjected to a calcination step in a muffle furnace at 850 °C for about 8 h.

Table 1. Elemental and proximate analysis of Harbul, Avgamasya and Segürük asphaltites

	Weight, %		
	Harbul	Avgamasya	Segürük
Elemental analysis:			
Carbon	54.079	51.436	46.775
Nitrogen	0.764	0.910	0.762
Hydrogen	5.122	3.868	4.406
Proximate analysis:			
Moisture	0.630	1.260	0.620
Ash	32.490	39.070	40.800
Fixed Carbon	20.140	25.080	24.860
Volatile mater	46.740	34.590	33.720
Heating value, kcal g ⁻¹	6276.253	5630.318	5430.827

Digestion procedures and measurement

Asphaltite bottom ash (ABA) samples were digested using the Berghof MWS-3 model microwave digestion system. The two-stage digestion was carried out as follows: 0.2-g portion of dried sample was weighed and transferred into a pressure-resistant PTFE vessel, and the mixture of acids (HNO₃, 65% +HF, 40%, 7:2 ml) was added. The vessel was closed and heated in the microwave oven with the program as given in Table 2. The vessels were

removed and carefully vented in a fume hood after cooling to room temperature in a water-bath. After the venting procedure mentioned above, 15 ml of boric acid (H_3BO_3 , saturated solution) was quickly added to each sample. Crystallisation of CaF_2 is avoided by addition of boric acid. The vessels were returned to the microwave oven, and the second processing was applied to the samples under the same temperature program as above. The reaction mixture was subjected to an evaporation procedure by use of the evaporation module in order to remove the acids after the final digestion. Then the residue was dissolved in Milli-Q water and filtrated, and the filtrate was diluted to 50 ml. The ICP-OES and FAAS measurements were performed for the diluted solutions. A total of 12 samples were evenly spaced in the microwave oven carousel and the MW-AD procedure was applied.

Table 2. Operating conditions for two-stage digestion by microwave oven

Step 1	1	2	3
T C	140	160	190
Ta (min) ^a	5	3	5
Time (min) ^b	5	10	20
Step 2	1	2	
T C	160	100	
Ta (min) ^a	3	1	
Time (min) ^b	15	15	

^a Waiting time at desired temperature

^b The time between the two sequential temperatures

Reagents and instrumentation

Nitric acid (HNO_3 , 65%), hydrofluoric acid (HF, 40%) and boric acid (H_3BO_3 , saturated solution) were analytical-grade reagents. Distilled water was further purified by a Milli-Q system and used throughout the experiments. For determination of vanadium in ABA digested samples, MW-AD followed by FAAS (ATI Unicam 929 model) and ICP-OES (Perkin Elmer Optima 2100 DV) were used. Coal Fly Ash Certified Reference Material NCS ZC78001 was used to check the accuracy of the analytical method used. The results of V determination were as follows (in $\mu\text{g g}^{-1}$, dry wt.): 95 (certified), 94 ± 0.72 (ICP-OES found), 94 ± 2 (FAAS found).

Results and discussion

The asphaltite samples for determination of V in asphaltite bottom ash were collected from Harbul (Silopi), Avgamasya and Segürük (Sirnak) deposits of SE Anatolia of Turkey. The combustion of these asphaltites produces fly and bottom ashes that are characterized by a high content of valuable elements

such as vanadium, nickel, molybdenum, uranium, thorium, sulfur and non-burnt carbon [7, 8]. Present primary resources are insufficient to satisfy V demand and, in order to alleviate insufficient domestic resources supply, many countries comprehensively utilize secondary resources containing V [24]. The remainder asphaltite bottom ashes are not only of economic but also of environmental concern. Exposure to V may cause coughing, bronchial irritation, gastrointestinal diseases and conjunctivitis [25].

The sample preparation method developed in this study for V determination in asphaltites by spectroanalytical technique includes dry ashing and wet acid microwave digestion.

Two atomic spectrometric techniques have been used: AAS and ICP-OES. Instrumental parameters are listed previously [7, 18, 21]. The estimated instrumental detection limit for V is in the range of 0.01 mg L^{-1} , which obviously has to be qualified because of the inevitable dilution of oil samples and the effect of the organic matrix on the overall performance of ICP-OES. The results are shown in Table 3. The results indicate that V content of both asphaltite veins clearly depends on the total concentration of vanadium in the region. As can be seen in Table 3, the content of V was the highest in the Avgamasya vein (Sirnak) asphaltite bottom ash, Harbul (Silopi) being the second and Segürük (Sirnak) the third one. Compared to AAS, ICP-OES offers a wider linear dynamic range and multielement detection capability, while AAS is basically a monoelement technique. The line at 292.464 nm about 0.01 mg L^{-1} sensitivity was used, as it has the highest sensitivity and the greatest freedom from interference effects, using equipment with good resolution of ICP-OES. The method was validated through the analysis of an SRM with good recoveries. Dry ash and microwave acid digestion method had clear advantages in terms of simplicity of sample preparation, overall analysis time, and the use of inorganic standards for calibration instead of expensive metalorganic standards.

Table 3. Comparison of the analytical results for determination of V in asphaltite bottom ash by ICP-OES and AAS

Asphaltite bottom ash	ICP-OES, g kg^{-1} (292.402 nm)	FAAS, g kg^{-1} (318.5 nm)
Segürük	2.777 ± 0.015	2.729 ± 0.049
Harbul	4.324 ± 0.039	4.301 ± 0.075
Avgamasya	5.871 ± 0.055	5.812 ± 0.089

The ore grades range from 0.09% to 2.35% V_2O_5 in various regions. The deposits mainly consist of a complex vanadium-bearing iron ore. Interesting source of vanadium is the treatment of bottom ash produced by the combustion of asphaltite. The bottom ash content of Avgamasya, Harbul and Segürük asphaltites was 5.871, 4.324, 2.777 g kg^{-1} (ICP-OES analysis) and

5.812, 4.301, 2729 g kg⁻¹ (FAAS analysis), respectively. V concentration is the highest in the Avgamasya asphaltite while the lowest in the Segürük asphaltite. One tonne of asphaltite bottom ash contains up to 5871 g, 4324 g, 2777 g vanadium within Avgamasya, Harbul, Segürük veins, respectively. Laboratory tests indicate that the asphaltite bottom ash is suitable as an economic source of V concentrate because of high content.

Conclusions

Determination of V in Turkish asphaltites was carried out.

The sample preparation method was developed for V determination in asphaltite by spectroanalytical techniques, dry ashing (at 850 °C) and wet acid digestion (HCl+HNO₃+H₃BO₃). MW-AD followed by ICP-OES and FAAS were used for the determination of V in asphaltite bottom ash. The results indicated that there were no significant differences between the comparative results. The results are in good agreement with the reference values. The common grade of V in processed ores is usually less than 2%. SE Anatolia asphaltite bottom ash, such as Avgamasya vein, can contain up to 5.871 g kg⁻¹ of vanadium. Consequently, asphaltite bottom ash is an economically suitable source of V.

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