

Comparison of Three Sequential Extraction Methods for the Determination of Iron, Manganese, and Thallium in Asphaltite Samples

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ABSTRACT: Asphaltite, which is based on petroleum, contains many elements that exist in different forms. In this study, the BCR sequential extraction (BCRSE), Tessier sequential extraction (TSE) and Stover sequential extraction (SSE) procedures were applied for the determination of Fe, Mn and Tl in different forms (exchangeable, carbonates, bound to organic and sulfide, and residual content) in the structure of asphaltite. The statistical relations between the metal values of the three different methods were determined and recommendations are given for the enrichment of these economically valuable elements from asphaltite samples. The most abundant form of Fe (%), Mn (mg kg⁻¹) and Tl (mg kg⁻¹) follows the order: reducible (2.28), residual (75.85) and residual (81.99) with BCRSE method; carbonates (2.46), residual (79.21) and residual (79.75) with TSE method; carbonates (2.36), residual (67.34) and residual (46.93) with SSE method. The Fe, Mn and Tl speciation scheme gives quantitative knowledge of toxicity, bioavailability, mobility, leachability and bioaccumulation, etc., for asphaltite. A comparison of the three methods shows that the TSE method is shorter and more economical, while SSE gives more detailed information about the chemical structure of the substances, and the BCRSE has reducible (as oxides) fractions for the metals. This is the first time that a comparison of the three extraction methods was carried out on asphaltites and reported. The certified reference material (CRM) NIST-1633b Coal Fly Ash was used to verify the accuracy of the method, and whether the results are in good agreement with the certified values.

Extraction Methods	Fraction (S)	Nominal Fraction
BCRSE	Step 1	Exchangeable + water and acid-Soluble (Carbonates)
	Step 2	Reducible (Fe-Mn oxides)
	Step 3	Oxidable (Bound to organic and sulfide)
	Step 4	Residual content
TSE	Step 1	Exchangeable
	Step 2	Carbonates
	Step 3	Oxidable (Bound to organic and sulfide)
	Step 4	Residual content
SSE	Step 1	Exchangeable
	Step 2	Sorbed
	Step 3	Organic bound
	Step 4	Carbonates
	Step 5	Sulfides
	Step 6	Residual

INTRODUCTION

Asphaltites are unique natural raw materials and one group of solid natural bitumens.¹ In the depths of the earth's crust, asphaltite is found in the liquid or semi-liquid state. Under the effects of hydrostatic pressure, gravitation, temperature, etc., asphaltites settle in the cracks and cavities of the earth, and contains 1.2% water, 4-7% sulfur and 35-40% ash.² Most asphaltite veins were formed in the Mesozoic-Cenozoic Era in SE Turkey. They contain large quantities of authigenic minerals similar to those precipitating within black shale, including clay minerals, quartz, albite, orthoclase and framboids of pyrite.³ It has a high thermal

value, contains rare minerals and is used as solid fuel. Besides, it is suitable as a raw material for synthetic oil production.⁴ Turkey has asphaltite reserves totaling about 82 million tons.⁵

Some elements in asphaltites are potentially hazardous to the environment and some of them are highly carcinogenic and bioaccumulate in the body. Therefore, knowing the various forms of the elements and their oxidation states is very important. Speciation analysis is defined by IUPAC as the analytical activity involved in identifying and/or measuring the quantities of one or more individual chemical species in a sample.⁶ The definition of species is based on several different levels of the atomic and

molecular structure where chemical forms of the same element are manifest.⁷⁻¹²

Thallium is obtained as a by-product during the production of basic metals such as zinc. It acts together with cadmium during the production of zinc. Cadmium and thallium are separated by the distillation method. Thallium is also a very toxic element. It is used in agriculture, pharmacy, photography, electrical industry, production of various corrosion-resistant alloys and thermometer production.^{13,14} Twenty-five elements together with Tl were investigated and they can be found in coal in appreciable concentrations. The mode of occurrence of Tl is associated with pyrite. The mode of occurrence of Mn is in the form of carbonates, siderite and ankerite.¹⁵ It is an essential trace element known to be related particularly to the reproductive functions. Deficiency may lead to brain damage, teratogenicity, skeletal abnormalities, and abnormal metabolism of lipids and carbohydrates. Miners exposed to chronic Mn overload show symptoms of the extrapyramidal system, surprisingly similar to patients with Parkinson's disease. For this reason, Mn can become a highly toxic heavy metal, emitted from industrial sources, and seriously damage human health, affect the ecosystem and accumulate in the food chain.^{16,17}

Iron is abundant in the earth's crust and occurs naturally in the aquatic environment; however, concentrations can be elevated due to human activities. Mining activities that expose pyrite and other sulfidic minerals to air and water lead to oxidation and release of iron and sulfuric acid in a process known as acid mine drainage (AMD).¹⁸

Although assessment of the total concentration of Fe and Mn in asphaltite is still useful in many areas, knowledge of their speciation is of primary importance because of their characteristic toxicity, mobility, bioavailability, and bioaccumulation depending on their different chemical fractions. The ICP-OES procedure is the most simple and reliable analytical method in the aqueous or solution phase for the elemental analysis of asphaltite due to its high selectivity and low interference problems.⁸ Electrothermal atomic absorption spectroscopy (ETAAS) with a graphite furnace, X-ray fluorescence (XRF) and atomic absorption spectrometry (AAS) have also been used to determine Fe, Mn and Tl. Assessment of the chemical and morphological structure of asphaltites is important for their effective management.

The aim of the present research was to investigate the total concentration and distribution of Fe, Mn and Tl (water-soluble, exchangeable, carbonate, reducible, oxidizable, sulfide and residual fractions) in asphaltite ash samples obtained at Şırnak-Karatepe, SE Turkey, and using the BCRSE, TSE and SSE extraction methods and analysis by ICP-OES. According to our literature survey, this comparison of the three sequential extraction methods and their speciation has not been reported previously.

EXPERIMENTAL

Reagents and Instrumentation. Reagents were of Suprapur, when available, or analytical grade (Merck, Germany) and used without further purification. Deionized distilled water was used throughout and obtained directly with a Milli-Q system (resistivity: 18.2 MΩ cm at 25°C, Millipore Corporation, USA). Nitric acid (HNO₃ 65%), hydrofluoric acid (HF 40%) and boric acid (H₃BO₃, saturated solution) were of analytical grade reagents.

A Berghof MWS-3 model microwave digestion system (Berghof Co., Germany) was used for acid digestion of the asphaltite ash. The determination of Mn, Fe and Tl was performed with a model Optima™ 2100 DV inductively coupled plasma optical emission spectrometer (ICP-OES), (PerkinElmer, Inc., USA). Selection of the instrumental parameters and optical wavelength was based on obtaining good sensitivity, reasonable detection limits, and eliminating interferences. The limits of detection (LOD) for Mn, Fe and Tl in ICP-OES were calculated as the concentration equal to 10 times the standard deviation of the background signal (the signal of the blank solution), which was multiplied by the dilution.

Sample preparation. The Karatepe flat is located in Karatepe, Şırnak, SE Anatolia, Turkey, near settlement areas. Its geographical coordinates are 44°52'15" N, 20°38'25" E, and is about 2.3 km in length. Four inclined boreholes with a total depth of 307.3 m were drilled, 2950 m long and 1.50 – 12.00 m wide (average 5.50 m). The asphaltite samples were obtained from a depth of 200 m. Samples in the amount of about 20.0 g were collected and dried in a Memmert ULM 500 drying oven (Germany) at 105°C, crushed in a Retsch BB1/A jaw crusher (Germany) and milled in a Retsch SRZ rotor beater mill. The particle sizes of the samples were sieved to a size of less than 100 µm. The ash content, heating value, moisture and volatile matter contents of the samples were then determined according to the ASTM standard.¹²

For analysis, 20.0 g of asphaltite sample was weighed into a porcelain vessel and subjected to a muffle oven calcination at 800°C over a period of about 6 h. The chemical analysis results of the asphaltite sample were obtained by a Carbolite brand (Serial no: 21-203261) ash furnace at 800°C. According to the results of this analysis, the asphaltite sample had a high ash content of 48.51% and a low-calorie value. Afterwards, the elemental composition (C, N, H) of the asphaltite samples was determined using a Carlo Erba elemental analyzer EA 1108. **Table 1** lists the elemental and proximate analysis of the Karatepe, Şırnak, asphaltite.

Digestion procedure. Acid digestion of asphaltite incineration residues was performed with a Berghof MWS-3 microwave digestion system. In this process, microwave acid digestion was performed in two stages and five steps. Approximately 0.2 g of the

Table 1. Elemental and Approximate Analysis of Karatepe, Şırnak, Turkey, Asphaltite

<i>Elemental analysis</i>	Content
Carbon (%)	45.416
Nitrogen (%)	1.085
Hydrogen (%)	4.897
Fe (%)	6.12±0.35
Mn (mg kg ⁻¹)	126±5
Tl (mg kg ⁻¹)	91.76±2.65
<i>Proximate analysis</i>	
Moisture (%)	0.602
Ash (%)	48.51
Volatiles (%)	16.03
Total Sulphur (%)	4.062
Lower Heat Value (Kcal g ⁻¹)	3614

Table 2. Analytical Results of CRM NIST-1633b by the Proposed method

Element	Certified Value	Our value	Recovery (%)
Fe (%)	7.78±0.23	7.80±0.05	100.38
Mn (mg kg ⁻¹)	131.8±1.7	129.7±0,9	98.41
Tl (mg kg ⁻¹)*	5.9	6.0	101.7

dried sample was weighed and transferred to a pressure-resistant polytetrafluoroethylene (PTFE) vessel. Then, a mixture of 10 mL HNO₃ and 3 mL HF acid was added to the material, the vessel closed and mounted in a sleeve for one hour. After removal, it was cooled to room temperature in a water bath. With the exception of the digestion program, the first stage of the method and the acid composition was the same as the one used for single-stage digestion. A 20 mL amount of H₃BO₃ reagent was added to the sample and the vessel returned to the microwave digestion system. The reaction mixture obtained after final digestion was subjected to an evaporation system to remove the acids.¹⁰ Subsequently, the residue was dissolved in water, filtered and the filtrate diluted to a constant volume of 50 mL with demineralized water.⁸ The NIST-CRM 1633b constituent elements in Coal Fly Ash (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used to check the accuracy of the analytical method. The results are listed in Table 2.

Analytical Procedure. The limits of detection (LOD) and limits of quantification (LOQ) for each metal were determined as follows: 10 independent analyses of a blank solution, spiked with the metal at a level of lower concentration of the analytical curve, were performed. The LOD and LOQ were calculated from the standard deviation (σ) of these determinations (LOD = 3 σ and LOQ = 10 σ). Table 3 lists the analytical performance results of ICP-OES.

Table 3. Analytical Performance of the Proposed Method

Element	Linear Range ($\mu\text{g kg}^{-1}$)	Regression	Correlation coefficient (R²)	LOD ($\mu\text{g kg}^{-1}$)	LOQ ($\mu\text{g kg}^{-1}$)
Fe	0-100	y=127.61x+32.557	0.9995	4.16	13.85
Mn	0-100	y=1.0412x+0.291	0.9993	6.97	23.21
Tl	0-100	y=2.6203x+0.752	0.9989	8.92	29.70

Sequential extraction methods. The research by Tessier et al.¹⁹, Kersten and Forstner²⁰, and Salomons and Forstner²¹ was based on the work of the Commission of the European Communities Reference Bureau (BCR). Hullebusch et al.²², Jegadeesan et al.²³, and Lin et al.²⁴ used the sequential extraction method widely to evaluate the mobility of trace metals.

The extraction procedure used in the present study is based on the determination of metals using potassium nitrate (KNO₃), sodium pyrophosphate (Na₄P₂O₇), potassium fluoride (KF), nitric acid (HNO₃) and sodium ethylene-diamine-tetra-acetic acid (EDTA) reagents.²⁵

RESULTS AND DISCUSSION

This study presents the speciation of Fe, Mn and Tl in asphaltite from Şırnak-Karatepe, SE Anatolia, Turkey, by three different sequential extraction methods and a comparison of the results of these methods. The ICP-OES instrument was used for elemental analysis.

BCRSE method

The BCRSE method was used to study the Fe, Mn and Tl distribution in the Şırnak-Karatepe asphaltite samples. Four separate fractions (Exchangeable + water and acid-Soluble Fraction, Carbonates, Reducible (Fe-Mn oxides), Oxidizable (bound to organic and sulfide), residual contents were obtained. The operating conditions for the BCRSE method are listed in Table 4. In addition, the concentrations of the different Fe, Mn and Tl fractions were determined using the BCRSE procedure for asphaltite, and the results are listed in Table 4.

Results of BCRSE method

Speciation of Fe, Mn and Tl was carried out using a revised BCR method based on the sequential extractions from the asphaltite sample of Fe, Mn and Tl forms: exchangeable, reducible, oxidizable, and residual fractions.

When Table 4 is considered, it was observed that the Fe content was between 0.19% and 2.28%, and the Mn content about 45.80 mg kg⁻¹ in the reducible fraction and 75.85 mg kg⁻¹ Mn in the highest residual fraction. On the other hand, the amount of Tl in the exchangeable, reducible and oxidizable fractions ranged from about 3.17 mg kg⁻¹ to 3.35 mg kg⁻¹, while the highest value in the residual fraction was about 81.99 mg kg⁻¹ Tl. Thus, one can conclude that 81.99 mg kg⁻¹ Tl in the analyzed asphaltite sample is high and can be recovered by enriching it economically, since it

Table 4. Operating Conditions and Concentrations of Fe, Mn and Tl in Asphaltite Found by BCRSE, TSE and SSE Methods (n=3)

Extraction Methods	Fraction (S)	Nominal Fraction	Extractants	Extraction Conditions	Fe (%)	Mn (mg kg ⁻¹)	Tl (mg kg ⁻¹)
BCRSE	Step 1	Exchangeable + water and acid-Soluble (Carbonates)	0.11 M CH ₃ COOH 40 mL (pH=7)	Shaken 16 h, 20 °C	0.19±0.02	1.26±0.11	3.17±0.14
	Step 2	Reducible (Fe-Mn oxides)	0.5M NH ₂ OH-HCl 40 mL	Shaken 16 h, 20 °C	2.28±0.36	45.80±1.15	3.25±0.19
	Step 3	Oxidable (Bound to organic and sulfide)	20 mL H ₂ O ₂ (30%) and then 50 mL 1 M NH ₄ CH ₃ COO	Shaken 1, 2, 16 h, 20, 85, 20 °C	1.53±0.24	2.09±0.15	3.35±0.20
	Step 4	Residual content	HCl/HNO ₃ (3:1) 10 ml demineralized water and 10 ml aqua regia	26 min, microwave oven	2.12±0.32	75.85±1.79	81.99±1.74
TSE	Step 1	Exchangeable	1M NH ₄ CH ₃ COO 10 ml	Shaken 1 h, 20 °C	0.14±0.03	1.43±0.16	1.57±0.22
	Step 2	Carbonates	1M CH ₃ COOH 10 ml	Shaken 1 h, 20 °C	2.46±0.29	43.74±0.59	6.89±0.19
	Step 3	Oxidable (Bound to organic and sulfide)	30% solution of H ₂ O ₂ (pH=2) 5 ml	Shaken 3 h, 35 °C	1.57±0.18	1.14±0.08	3.51±0.27
	Step 4	Residual content	HCl/HNO ₃ (3:1) 10 ml demineralized water and 10 ml aqua regia	26 min, microwave oven	1.92±0.24	79.21±0.92	79.75±1.63
SSE	Step 1	Exchangeable	1M KNO ₃ 30 mL	Shaken 16 h, 20 °C	0.09±0.01	0.87±0.06	1.79±0.13
	Step 2	Sorbed	0.5M KF 48 mL	Shaken 16 h, 20 °C	0.08±0.02	0.73±0.02	2.86±0.25
	Step 3	Organic bound	0.1M Na ₄ P ₂ O ₄ 48 mL	Shaken 16 h, 20 °C	1.07±0.06	0.92±0.04	3.98±0.18
	Step 4	Carbonates	0.1M EDTA 48 mL	Shaken 16 h, 20 °C	2.36±0.25	41.89±0.73	7.07±0.34
	Step 5	Sulfides	1M HNO ₃ 30 mL	Shaken 16 h, 20 °C	1.94±0.10	13.25±0.32	29.16±0.61
	Step 6	Residual	HCl/HNO ₃ (3:1) 10 mL demineralized water and 10 mL aqua regia	26 min, microwave oven	0.58±0.04	67.34±1.21	46.93±1.27

is known that ores containing 10 g t⁻¹ or 10 mg kg⁻¹ and higher in terms of thallium (Tl) can be enriched. Hence, it can be said that the Tl values obtained in the asphaltite samples by the BCRSE extraction method do not pose environmental risks.

TSE method

The TSE method was used to study the Fe, Mn and Tl distribution in the Şırnak-Karatepe asphaltite samples. The concentrations of the different Fe, Mn and Tl fractions were determined using the TSE procedure. The results and operating conditions for the TSE method are given in Table 4.

Results of TSE method

Fractionation of Fe, Mn and Tl was carried out using a modified Tessier method based on the sequential extractions from the asphaltite sample of the Fe, Mn, and Tl forms: exchangeable, carbonates, organic matter and sulfide, and residual fractions. When Table 4 is considered, it can be seen that the Fe concentration was between 0.14% and 2.46% and the Mn concentration was about 43.74 mg kg⁻¹ in the carbonate fraction, and highest at 79.21 mg kg⁻¹ in the residual fraction. Accordingly, it can be said that the amount of Mn obtained in the residual

fraction of the TSE method in the asphaltite sample appears within harmful limits; however, this value is within acceptable limits considering the Mn values in the soil and plant. In addition, the enrichment methods can be applied to this fraction to be gained in different sectors. When the Mn values of the other methods and other fractions are compared, it is seen that it is normal.

On the other hand, the amount of Tl varied between about 1.57 mg kg⁻¹ and 6.89 mg kg⁻¹ in the exchangeable, carbonates, organic matter-sulfide fractions, while the highest value in the residual fraction was about 79.75 mg kg⁻¹ Tl. It is known that ores containing 10 g t⁻¹ or 10 mg kg⁻¹ and higher in terms of Tl have economic value; hence, it was concluded that 79.75 mg kg⁻¹ Tl in the analyzed asphaltite sample is high and can be obtained by enriching it economically.

SSE method

The SSE method was used to study the Fe, Mn, and Tl distribution in the Şırnak-Karatepe asphaltite samples. The SSE method was applied with six different fractions (exchangeable, sorbed, organic-bound, carbonates, sulfides, and residual fractions). The concentrations of the different Fe, Mn and Tl fractions were determined using the SSE procedure. The operating conditions

and the experimental results are listed in Table 4.

Results of SSE Method

The fractionations of Fe, Mn and Tl were carried out using a revised Stover method based on the sequential extractions from the asphaltite sample of the Fe, Mn and Tl forms: exchangeable, sorbed, organically bound, carbonates, sulfides and residual fractions.

When Table 4 is considered, it can be observed that the Fe concentration as % varies from about 0.08% to about 2.36%. These ratios have no economic value for Fe enrichment. The Mn concentration was found to be about 13.25 mg kg⁻¹ in the sulfides fraction, about 41.89 mg kg⁻¹ in the carbonates fraction, and about 67.34 mg kg⁻¹ in the highest residual fraction. The Mn values in the exchangeable, sorbed, and organic-bound fractions ranged from about 0.73-0.92 mg kg⁻¹. Accordingly, the values in the asphaltite samples do not pose environmental risks.

On the other hand, the amount of Tl varied between about 1.79 mg kg⁻¹ to 7.07 mg kg⁻¹ in the exchangeable, sorbed, organic-bound and carbonates fractions, while that in the sulfide fraction was about 29.16 mg kg⁻¹, and the highest residual fraction was 46.93 mg kg⁻¹. As the ore containing 10 g t⁻¹ or 10 mg kg⁻¹ or higher in terms of Tl has economic value, it can be concluded that the Tl amount of 29.16 mg kg⁻¹ and 46.93 mg kg⁻¹ in the analyzed asphaltite sample is economically valuable, so it can be enriched.

Comparison of Fe, Mn and Tl element results according to BCRSE, TSE and SSE methods

If the concentration of heavy metals in fly ash is high, they can present significant hazards to soil and water environments. The environmental behavior of heavy metals in toxic trace amounts is evaluated differently. The weak acid-soluble and water-soluble fractions belong to mobile fractions or biologically available fractions. The less unstable forms of these metals (oxidizable and reducible fractions) are considered to be low mobile fractions. In this order, the environmentally stable fraction deserves to be called a very low mobile fraction.

When the Fe, Mn and Tl results of the BCRSE, TSE and SSE methods applied in the asphaltite sample were compared, it was observed that the % amount of Fe was between 0.08% and 2.46%. When considered in terms of ore enrichment, this trace amount of Fe % in mining is generally seen as undesired impurities. When the ratios of Mn (mg kg⁻¹) were compared, it was seen that the highest values of all methods and fractions were found in the residual fractions. The highest ratio of Mn in the residual fraction of the TSE method was obtained as 79.21 mg kg⁻¹. When the Tl (mg kg⁻¹) values were compared, it was observed that the highest values of all methods and fractions were found in the residual fractions. The ratio of Tl in the asphaltite sample was 46.93 mg kg⁻¹ with the SSE method and 81.99 mg kg⁻¹ with the BCRSE method.

Iron (Fe): Fe was the major element in our ash. In ash, the most

abundant form of Fe follows the order: reducible > residual > oxidizable > exchangeable in BCRSE, carbonates > residual > oxidizable > exchangeable in TSE, and carbonates > sulfides > organic-bound > residual > exchangeable > sorbed in SSE.

We think for BCRSE, the majority of Fe is present as the refractory species, such as hematite, magnetite and ferric/ferrous species in our sample.²⁴ However, Fe seemed to be as sulfate species, which may explain the fact that very little Fe (<0.2%) was present in the water/acid-soluble phase.²³ In the case of the TSE methods, our results are different from those in the fly ash from Poland.¹⁹

Manganese (Mn): The most abundant form of Mn follows the order: residual > reducible > oxidizable > exchangeable in BCR, residual > carbonates > exchangeable > oxidizable in Tessier, and residual > carbonates > sulfides > organic-bound > exchangeable > sorbed in the SSE method.

In all three extraction methods, the residual form is high for the value for Mn. This result is different from that found by Nilufer Ozcan and Huseyin Altundag,²⁶ but is the same as that of E. Varhan in BCR.²⁷ In the SSE method, the residue and sulfides values are high for Tl. This sequential extraction method gave detailed information on the chemical composition of ash.

Thallium (Tl): The most abundant form of Tl follows the order: residual > oxidizable > reducible > exchangeable > in BCRSE, residual > carbonates > oxidizable > exchangeable in TSE, and residual > sulfides > carbonates > organic-bound > sorbed > exchangeable in the SSE method. The results showed that the concentration of Tl in our samples was much higher in the residual fraction, and the exchangeable fraction was low for all extraction methods. For environmental pollution, this is a very important result.

CONCLUSIONS

The concentrations of Fe, Mn and Tl in the asphaltite ash samples (Karatepe, Şırnak, SE Anatolia, Turkey) were determined by BCRSE (for exchangeable, reducible, oxidizable and residual fractions), TSE (for exchangeable, carbonates, oxidizable and residual fractions), and SSE methods (for exchangeable, sorbed, organic bound, carbonates, sulfides and residual fractions). How metals bonded to the ore and the characteristics of the reactants are determined by the three methods.

The most abundant form of Fe follows the order: reducible > residual > oxidizable > exchangeable in BCRSE, carbonates > residual > oxidizable > exchangeable in TSE, and carbonates > sulfides > organic bound > residual > exchangeable > sorbed in the SSE method.

The order for Mn follows: residual > reducible > oxidizable > exchangeable in BCRSE, residual > carbonates > exchangeable > oxidizable in TSE, and residual > carbonates > sulfides > organic

bound > exchangeable > sorbed in the SSE method.

Tl follows the order: residual > oxidizable > reducible > exchangeable > in BCRSE, residual > carbonates > oxidizable > exchangeable in TSE, and residual > sulfides > carbonates > organic-bound > sorbed > exchangeable in the SSE method.

It is understood that the harmful metals in asphaltite ash do not dissolve in water, and at pH 3-7 there is not much harm to the environment. However, this work and to recover these precious metals, especially Tl and Mn, should be performed soon since it will contribute greatly to the national economy.

In conclusion, we would like to make the following remarks for comparison of the three sequential extraction methods: Compared to the other methods, the TSE method requires less time and is more economical, while SSE gives more information about the chemical structure of the substances. Although the BCRSE method is more time-consuming, it provides information about the reducible form of the metals. The SSE procedure gives more detailed fraction and decomposition knowledge and is, therefore, more suitable for asphaltite.

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Notes

The authors declare no competing financial interest.

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