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REVIEWS

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## Present-Day Methods for the Determination of Trace Elements in Oil and Its Fractions

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**Abstract**—The development and use of instrumental methods for the determination of a wide range of trace elements in oil is considered. Special attention is paid to methods of the direct introduction of samples into spectrometers. It is shown that preliminary sample preparation is in certain cases necessary for the determination of trace elements in oil. The main methods of sample preparation of oils, including methods of extraction of a series of trace elements from crude oil (extraction, membrane, sorption, etc.), are described.

**Keywords:** oil analysis, microelemental composition, instrumental methods of analysis, sample preparation

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Oil is a complex multiphase natural system, including not only of hydrocarbon and heteroatomic components, but also more than 60 trace elements (TEs). The concentrations of elements in oil are distributed as follows [1, 2]: concentrations of V and Ni vary within  $10^{-3}$ – $10^{-1}\%$ ; Fe, Mo, As, Co, Cu, Mn, Sr, Se, and Rb, within  $10^{-5}$ – $10^{-3}\%$ ; and Sn, Ag, In, Re, Au, Os, Ir, Pd, Pt, Be, Sc, Ga, Ge, Sb, La, Ti, Hg, Bi, Cd, Yb, W, etc., lower than  $10^{-5}\%$ . However, concentrations of some elements, such as Fe, V, and Ni, in high-viscosity oils and natural bitumens can be quite substantial and higher than 0.1%. In addition, some oil fields with abnormally high concentrations of platinum and rare-earth elements (REE) are known. Oil from such fields can be considered an alternative source of metal production [3–5].

Trace elements in oils are usually determined in solving various geological and geochemical, industrial raw, and technological and environmental problems [6]. The ratio of some TEs in oil gives information about its origin, migration processes, and often determines the strategy of oil field exploration [7, 8]. On the other hand, some TEs (V, Ni, Fe, As, Se, etc.) even in insignificant amounts substantially damage industrial equipment, causing corrosion and failure of the main units of oil refining plants; poison catalysts of crude oil processing; and reduce the quality of commercial petroleum products [9]. In addition, some compounds of trace elements (V, Co, Ni, Cr, Mn, Cu, Zn, As, Se, Tl, F, Be, Cd, Hg, Pb, Sn, Mo) are highly toxic substances, dangerous both for the environment and human health [10]; their emissions to the atmosphere significantly complicate the environmental situation in oil production areas.

The speciation of trace elements and their concentrations in oil raw materials vary significantly and depend on the characteristics of oil fields. According to the data [11–13], most of TEs in oils occur as organoelement compounds of porphyrins (V, Ni, Fe, Cu), nonporphyrin complexes (V, Ni), and naphthenates (alkali metals, Ca, Mg, Zn, Ti). Note that there is virtually no information on the structures of organic compounds of vanadium and nickel of the nonporphyrin series, in spite of the fact that their concentrations in oil can be significant. Nonporphyrin compounds may contain ligands of pseudoporphyrin structure with enhanced aromaticity and/or element complexes with tetradentate ligands bearing various donor atoms. Porphyrins are compounds in which four pyrrol rings are bound by bridges into a cyclic conjugated system with a 16-membered macrocycle, including four nitrogen atoms.

It is supposed that the most part of TEs is concentrated mainly in asphaltic–resinous fractions of oil [2]. A group of trace elements (Pb, Ba, Sn, Ag, Co, Mo, Ti, Zn, Cu, Hg, Se, As) was found in the lube fraction of oil. These elements form either organometallic compounds, for example, alkylmercury  $\text{Hg}(\text{Alk})_2$ , aryl- and alkyllead  $\text{Pb}(\text{Alk})_4$ , or complexes with different organic ligands occurring in oil.

A number of normative documents were developed for the determination of the elemental composition of oils: *GOST* (State Standards), *UOP* (Universal Oil Products), *ISO* (International Organization for Standardization), *ASTM* (American Society for Testing and Materials). A substantial number of standard analytical procedures were proposed for the determination of TEs in commercial products, motor fuels,

lubricant oils, light distillates, etc. The choice of standard procedures for the analysis of crude oils is very limited. This is due to, first of all, that oil is a complex multicomponent system, characterized by different values of density and viscosity and a diversity of element species in its composition [14–21]. A review of some standard procedures for the determination of elements developed for crude oils is provided in Table 1. Note that the majority of certified analytical procedures for the study of oils are intended for single-element analysis or for the determination of a quite narrow range of elements. As can be seen in Table 1, only atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission (optical emission) spectrometry **ICP AES (ICP OES)**, and spectrophotometry were recommended as standard methods of analysis for the determination of TEs in oils. Note also that the specified analytical procedures require sufficiently complex sample preparation.

Every year new analytical instruments with improved characteristics in sensitivity to analytes in different matrixes appear in the market. Note that the instrumental determination of elements in oils because of the complexity (wide variety of element species) and diversity (significant difference in physical and chemical properties) of the studied samples is virtually impossible without sample preparation. The known direct methods of oil analysis (sample introduction directly into the spectrometer) require either the dilution of the analyzed sample or the introduction of special modifiers.

The problem of the determination of TEs in oil products, including the stage of sample preparation to analysis, was discussed in a number of publications [1, 9, 11, 22–28]. In this review, we consider present-day methods for the determination of TEs in oil and different versions of oil sample preparation to instrumental analysis. Special attention is paid to a possibility of the direct analysis of oils (test sample introduction into the spectrometer).

#### METHODS FOR THE DETERMINATION OF TRACE ELEMENTS IN OIL

Among the present-day analytical methods for the determination of TEs in crude oil and petroleum products differing by high sensitivity, selectivity, and, in many cases, productivity, let us note electrothermal atomic absorption spectrometry (**ETAAS**), inductively coupled plasma mass spectrometry with (**ICP MS**), and ICP AES (**ICP OES**) [22–25, 28]. Table 2 presents published data on the determination of trace elements in oils and characteristics of the used methods of oil analysis. By the direct method of determination we mean the direct introduction of a sample diluted with solvents or a sample emulsion into the analytical instrument and also direct introduction into the analyzer on a platform or in another holder. Brief descrip-

tions of each method of analysis and corresponding methods of sample preparation are given below.

#### **Electrothermal atomic absorption spectrometry.**

The ETAAS approach ensures the attainment of limits of detection (LODs) for some elements in liquid samples down to  $n \times 10^{-3} \mu\text{g/L}$ . The performance characteristics of the method were improved through the development of the STPF furnace (Stabilized Temperature Platform Furnace); use of graphite furnaces, platforms coated with pyrolytic graphite; background correction (optical systems with two light sources, Zeeman background correction); new radiation sources (continuous spectrum, lasers); matrix modifiers; etc.

Electrothermal atomic absorption spectrometry has still been a method of single-element analysis, except for cases when continuous light sources are used. The method is characterized by low productivity, strict requirements to experimental conditions and the selection of a modifier, expensive consumables, need in the use of reference materials and instrument calibration, etc. In the use of graphite furnaces, there arise problems with the determination of Hf, Nb, Ta, W, and Zr, forming hardly volatile carbides with carbon as a result of pyrolysis.

An advantage of the method is a possibility of direct sample introduction into a spectrometer or an atomizer without additional sample preparation. The method of direct sample introduction into an electrothermal atomizer ensures the determination of TEs in high-viscosity the oils and fuel oil. It also offers a possibility of the reduction of the time of sample preparation to analysis and of prevention of its pollution and losses. The advisability of using of aqueous inorganic reference materials instead of expensive organometallic ones for the construction of calibration curves was proved in the works on the direct analysis of oils by ETAAS [29–34]. Unfortunately, despite the high promise of the direct analysis of complex samples, this method has still remained at a level of research. It requires a careful choice of modifiers, temperature program, and corresponding calibration of the instrument. Because of the complexity of the process of homogenization of high-viscosity samples and low concentrations of analytes in the analytical weighed portion, the observed measurement errors varied from 5 to 25% [29–31]. The addition of a modifier to the test sample allows the researcher to change the thermal stability of analyte compounds, reduce their losses, improve separation from the matrix, and also favors the transfer of analytes into one compound, which considerably reduces hindrances and simplifies the interpretation of the results of measurement in the analysis of oils, including high-viscosity ones [31, 32, 75, 76].

Silva with coauthors in [33] showed a possibility of the determination of the total concentration of vanadium and nickel, and also of their thermally stable and

**Table 1.** Standard methods of the determination of trace elements in crude oil

Method of analysis	Standard documents	Analytes
Atomic absorption spectrometry	<i>ASTM D7622-10</i> (2015) Standard Test Method for Total Mercury in Crude Oil Using Combustion and Direct Cold Vapor Atomic Absorption Method with Zeeman Background Correction [14]	Hg
	<i>ASTM D7623-10</i> (2015) Standard Test Method for Total Mercury in Crude Oil Using Combustion-Gold Amalgamation and Cold Vapor Atomic Absorption Method [15]	Hg
	<i>ASTM D5863-00a</i> (2011) Standard Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry [16]	Ni, V, Fe, Na
	<i>UOP 391-09</i> Trace Metals in Petroleum Products or Organics by AAS [20]	Fe, Ni, V, Cu, Na, K
	<i>ASTM D7691-11e1</i> Standard Test Method for Multielement Analysis of Crude Oils Using Inductively Coupled Plasma Atomic Emission Spectrometry ICP AES [17]	Fe, Ni, V
Inductively Coupled Plasma Atomic Emission Spectrometry	<i>ASTM D5708-15</i> Standard Test Methods for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry [18]	Ni, V, Fe
	<i>UOP 389-15</i> Trace Metals in Organics by ICP OES [19]	Al, Ca, Co, Cr, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, Pd, P, Pt, K, Na, Sr, Sn, Ti, V, Zn
Photometry	<i>GOST</i> (State Standard) 10354-90: Oil and Petroleum Products. Method for Determination of Vanadium [21]	V

**Table 2.** Characteristics of instrumental methods for the determination of trace elements in oil and oil products using the direct introduction of the test sample into the spectrometer, its dilution by solvents, and emulsification

Analytes	Test sample	Method of sample preparation	Limit of detection, $\mu\text{g/g}$ ( $\mu\text{g/L}$ )	Reference
ETAAS				
Co, V	Crude oil	Direct introduction into an atomizer on a platform in the presence of a modifier (20 $\mu\text{g}$ of Pd in a 0.05% solution of Triton X-100)	Co 0.008 V 1.2	[29]
Cr, Fe	The same	Direct introduction into an atomizer on a platform without a modifier	Cr 0.001 Fe 0.6	[30]
Ni, V	"	As an emulsion: 0.05–2 g of sample–1 mL of xylene–100 $\mu\text{L}$ of Triton X-100–water (to a volume of 10 mL); US homogenization; presence of a modifier: 20 $\mu\text{L}$ of Pd solution	Ni 0.02 V 0.06	[31]
Ni, Pb	Petrol, diesel fuel	As an emulsion sample–propanol–50% $\text{HNO}_3$ (3.3 : 6.5 : 1); with the addition of a modifier for the determination of Pb	Ni 4.5 Pb 3.6	[32]
Ni, V	Crude oil	Direct introduction into an atomizer on a platform in the presence of a modifier (40 $\mu\text{L}$ of a Pd solution, 0.5 g/L in a 0.05% solution of Triton X-100)	Ni 0.02 V 0.06	[33]
Cu, Fe, Cr	The same	Direct introduction into an atomizer on a platform in the presence of a modifier (20 $\mu\text{L}$ of a 1500 $\mu\text{g/mL}$ solution of Pd, 0.1% $\text{HNO}_3$ in a 0.025% solution of Triton X-100)	Cu 3–100 Fe 70–2000 V 27–8000 (sample weight 0.1–3 mg)	[34]
Ni, V	"	Direct introduction into an atomizer on a platform in the presence of a modifier (20 $\mu\text{L}$ of a 1500 $\mu\text{g/mL}$ or 1000 $\mu\text{g/mL}$ solution of Pd, 0.1% $\text{HNO}_3$ in a 0.025% solution of Triton X-100)	Ni 0.09 V 0.1	[35]
Pb	"	Direct introduction into an atomizer on a platform in the presence of a modifier (20 $\mu\text{L}$ of a 20 $\mu\text{g}$ solution Pd, 6 $\mu\text{g}$ of Mg in a 0.05% solution of Triton X-100); introduction as an emulsion using a plug filter (0.5 g of sample, 1 mL of xylene, 100 $\mu\text{L}$ of Triton X-100, solution diluted to a volume of 10 mL with water; modifier: 10 $\mu\text{g}$ Pd, 3 $\mu\text{g}$ Mg)	0.004	[36]
V	Petrol, diesel fuel, condensate	As an emulsion conc. $\text{HNO}_3$ –Triton X-100–sample–water (1 : 1 : 2 : 6); two-step US treatment within 10 and 45 min	(14)	[37]
Co, Cu, Pb, Se	Oil, petrol, diesel fuel	As an emulsion 400 mg of sample–125 $\mu\text{L}$ of hexane–7.5 mL of Triton X-100–25 mL of water; 30 min of US treatment; addition of a modifier $\text{Pd}(\text{NO}_3)_2$ (10 $\mu\text{L}$ , 2 g/L)	Co 0.02 Cu 0.03 Pb 0.04 Se 0.11	[38]
V	Residual oil	As an emulsion: 0.1 g of sample diluted with 2 mL of xylene to reduce viscosity, then added 0.5 mL of conc. $\text{HNO}_3$ (5 min of US treatment); after US homogenization 0.6 mL of water and 2 mL of MIBK* were added to the solution and diluted it with propanol to 10 mL (homogenization within 1 min)	0.1	[39]
V, Ni, Co	The same	As a sample emulsion in toluene– $\text{HNO}_3$ –xylene–Triton X-100–water	V 5.7 Ni 6.6 Co 0.07	[40]

Table 2. (Contd.)

Analytes	Test sample	Method of sample preparation	Limit of detection, µg/g (µg/L)	Reference
Ni	Oil	As an emulsion 0.1–2 g of sample–1 mL of xylene–100 µL of Triton X-100–dist. water (volume brought to 10 mL); US homogenization; by diluting 0.1–2 g of sample with xylene or MIBK to a volume of 10 mL	0.07	[41]
V	Crude oil	As an emulsion 0.05–2 g of sample in 1 mL of xylene–100 µL of Triton X-100–water (to a volume of 10 mL); US homogenization; presence of a modifier: 20 µL of a Pd solution	0.04	[42]
V, Ni	The same	As an emulsion 25–300 mg of sample in 1 mL of xylene–100 µL of conc. HNO <sub>3</sub> –2 mL of 5% Triton X-100–water (to a volume of 10 mL); US homogenization; without a modifier	Ni 3 V 1	[43]
Pb	Petroleum condensate	Dilution with organic solvents – 3 mL of sample in 7 mL of xylene; Pd modifier	(0.8)	[44]
V	Heavy oils	Dilution with organic solvents: 0.1–5 g of sample diluted to 10 mL with a mixture of THF with light oil (1 : 1)	–	[45]
Cd, Cr, Cu, Pb, Ni	Petrol, diesel fuel	Dilution with organic solvents: diesel fuel–heptane (1 : 4)	Cd $1.3 \times 10^{-4}$ Cr $4 \times 10^{-4}$ Cu $9 \times 10^{-4}$ Pb $1.5 \times 10^{-3}$ Ni $2.5 \times 10^{-3}$	[46]
ICP AES				
Pb	Aviation fuel	Dilution with organic solvents: sample–toluene (1 : 99).	800 µg/L	[47]
Fe, V, Ni	Standard NIST samples (elements in HOR, residual oils, lubricant oils, oils)	Dilution with organic solvents: sample–tetraline (1 : 10).	$V 2 \times 10^{-3}$ $Fe 5 \times 10^{-3}$ $Ni 1.2 \times 10^{-2}$	[48]
Ba, Ca, Cd, Co, Cr, Cu, Fe, La, Mg, Mn, Ni, Pb, Ru, V, Y, Zn	Oil	Dilution with organic solvents: after distillation of fraction boiling below 140°C, sample diluted with xylene depending on the initial viscosity	0.001–0.1	[49]
Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn	Heavy oil residues	Dilution with organic solvents: 1 g of sample in 10, 30, 60 mL of xylene or toluene	0.01–4.5	[50]

Table 2. (Contd.)

Analytes	Test sample	Method of sample preparation	Limit of detection, µg/g (µg/L)	Reference
Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr, Co	Oil	As an emulsion sample—propanol—water—conc. HNO <sub>3</sub> (6 : 70 : 20 : 4); decomposition in the presence of HNO <sub>3</sub> and H <sub>2</sub> O <sub>2</sub> using microwave radiation	0.4–0.013	[51]
Mo, V, Cr, Ti	Diesel fuel	Emulsification with surfactant: sample in xylene—Triton X-100—water (5–15 : 3 : 92–82, by weight)	Mo 0.1 V 0.6 Cr 0.04 Ti 0.2	[52]
		Emulsification without surfactant: sample—propanol—water (25 : 60 : 15, by weight); addition of 0.5 mL of conc. HNO <sub>3</sub> for two methods of emulsification	Mo 0.8 V 0.2 Cr 0.05 Ti 0.4	
		Method of dilution with organic solvents: sample—kerosene (20 : 80), sample—xylene (10 : 90)	Mo 1.5 V 0.2 Cr 0.15 Ti 0.2	
Ba, Ca, Mg, Na	Oil	As an emulsion 200 mg of sample—1 mL of xylene—2 mL of 5% solution of Triton X-100 in 10% HNO <sub>3</sub> —water (to a volume of 10 mL); US homogenization followed by the break of emulsion at 80°C, separation in a centrifuge and analysis of the water phase	Ba (0.12) Ca (1.2) Mg (0.12) Na (5.8)	[53]
MP AES				
Ni, V, Fe, Ca	Oil	Dilution with organic solvents: sample—xylene (1 : 10, 1 : 20, 1 : 30)	Fe 0.09 V 0.04 Ni 0.03	[54]
LSES				
Ca, Fe, Mg, Zn, Cu, Ni, Mo	Oil residues	Direct introduction: HOR heated at 150°C and put into steel moulds 20 mm in diameter and 10 mm in height	2–14	[55]
Co, Fe, V, Ni, Pb, Mo, Ti, Mn, Cd, Cu	Asphaltenes	Direct introduction: asphaltenes under pressure are put into steel moulds 20 mm in diameter and 10 mm in height	2–10	[56]

Table 2. (Contd.)

Analytes	Test sample	Method of sample preparation	Limit of detection, $\mu\text{g/g}$ ( $\mu\text{g/L}$ )	Reference
Ni, V	Oil	Encapsulation in zirconia xerogel (multistep sample preparation)	V 7 Ni 4	[57]
ICP MS				
V, Ni, Co, Y, Mo, Cd, Ba, La, Ni, Fe, Zn, Sr, Sn, Pb, Ag, Al	Asphaltenes, maltene fractions	Dilution with organic solvents: sample-toluene (1 : 200)	(<0.1–1)	[58]
V, Ni, Cu, Mo, Ag, Sn, Ba, Pb, Cd	Oil, asphaltenes, maltenes	Dilution with organic solvents: sample-xylene (1 : 100)	$6 \times 10^{-6}$ – $2.29 \times 10^{-4}$	[59]
Ag, Al, Ba, Ca, Co, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sn, Ti, V	Oil	Dilution with organic solvents: 0.1 g of sample diluted with 10 g of xylene; addition of 5 g of xylene to 0.1 g of an aliquot portion	$1.8 \times 10^{-3}$ – $6.9 \times 10^{-2}$	[60]
V, Ni, Mo	The same	Dilution with organic solvents: sample-xylene (1 : 10)	$V 3 \times 10^{-4}$ $Ni 6 \times 10^{-4}$ $Mo 8 \times 10^{-4}$	[61]
ICP MS, ICP OES				
Fe, V, Ni, Ca	"	Dilution with organic solvents: sample-xylene (from 1 : 10 to 1 : 600 depending on the physico-chemical properties of oils)	$(0.22-2.16) \times 10^3$ (ICP MS) 0.02 for all elements (ICP OES)	[62]
Ba, Ca, Co, Cr, Cu, Fe, Sn, Mn, Mo, Ni, Pb, V, Zn et al.	Petrol	Sample-xylene (1 : 5, 1 : 50)	$<10^{-3}$ (ICP MS) $(1-30) \times 10^{-3}$ (ICP OES)	[63]
LA ICP MS				
V, Ni, Fe, Cr, Cu, Zn, Cd, Sn	Oil	0.1–0.2 g of sample were mixed with 0.2–1 mL of solution in MIBK containing a known amount of isotopes (isotope dilution) and placed on cellulose fixed in a PTFE** ring	0.02–0.21	[64]

Table 2. (Contd.)

Analytes	Test sample	Method of sample preparation	Limit of detection, µg/g (µg/L)	Reference
Ag, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V	Standard samples of oils, asphaltens, lubricants	Sample was diluted with THF*** (1 : 200 or 1 : 500) and placed on a chromatography plate (silica)	0.0012–0.16	[65]
V, Ni	Oil	Sample was introduced as a xerogel	Ni 0.7 V 0.8	[66]
V, Ni, Mo, Pb	The same	Sample was placed in a special glass cylinder with a cover	$5 \times 10^{-3}$ Ni $8 \times 10^{-3}$ Pb $0.6 \times 10^{-3}$ Mo $2 \times 10^{-3}$	[67]
Na, Mg, Al, Pb, Ag, Cu, Co, Ni, Fe, Cr, Ti	Lubricants	Direct introduction	0.0005–0.028	[68]
ET ICP MS				
Cu, Mn, Ni, Sn	Petrol	As an emulsion 1 mL of sample–0.5 mL conc. HNO <sub>3</sub> –100 µL Triton X-100–8.5 mL of water; US homogenization; modifier	Cu (0.22) Mn (0.02) Ni (0.38) Sn (0.03)	[69]
XRF				
Ca, Fe, Ni, V	Oil, HORS		Ca 2.1 Fe 2.2 Ni 1.7 V 1.9	[70]
Fe, Cu	Petrol		Fe (10) Cu (15)	[71]
Fe, Zn, Pb, Cu, Cr	Lubricants		Fe 1.2 Zn 1.24 Pb 7.11 Cu 2.13 Cr 1.76	[72]
Ni, V	Crude oil, bitumens, asphaltens		V 5	[73]
V, Fe, Ni	Oil		Ni 2 V 0.6 Ni 0.4 Fe 0.1	[74]

\* Methyl isobutyl ketone, \*\* polytetrafluoroethylene, \*\*\* tetrahydrofuran.



volatile species in samples of crude oil without additional sample preparation using single-element radiation sources, hollow cathode lamps. In the analysis of samples they used a modifier (Pd in a 0.05% solution of Triton X-100) to stabilize volatile compounds of vanadium and nickel. The concentration of volatile element compounds was calculated as a difference between the results of determination with and without the addition of the modifier to the analyzed sample. The accuracy of element determination by the proposed method was confirmed by the analysis of certified reference materials NIST SRM 1634c (trace metals in fuel oil). The authors confirmed that the results of experiment were comparable with the results of AAS using a continuous spectrum source and sample introduction into the furnace as an emulsion. The limits of detection for nickel and vanadium were 0.02 and 0.06  $\mu\text{g/g}$ , respectively, at a test sample portion of 10 mg.

Vanadium and cobalt were simultaneously determined in five samples of crude oil by ETAAS with a continuous spectrum source (xenon arc lamp) using palladium in a 0.05% solution of Triton X-100 as a modifier [29]. Oil samples were homogenized on an ultrasonic (US) setup within 10 min and, after the addition of the modifier, placed in a graphite tube of a platform atomizer. The limits of detection for vanadium and cobalt were 1.2 and 0.008  $\mu\text{g/g}$ , respectively. The accuracy of the method was confirmed by the analysis of certified samples NIST SRM 1632 (REE in fuel oil). Dittert et al. in [30] published data on the simultaneous determination of chromium and iron in samples of Venezuelan and Brazilian oil by ETAAS (without modifiers).

Brandão et al. in [34] determined concentrations of Cu, Fe, and V in samples of crude oil in the presence of a palladium modifier in a 0.1%  $\text{HNO}_3$  solution and in a 0.025% solution of Triton X-100. Vieira with coauthors [35] determined vanadium and nickel in 64 samples of Brazilian oil differing in density and viscosity.

In [36] lead was determined in crude oil by ETAAS in two versions: direct sample introduction into a system with a modifier (Pd + Mg in a 0.05% solution of Triton X-100) and as an emulsion sample-xylene-Pd + Mg-0.05% solution of Triton X-100-water using a graphite plug filter. The limits of detection for both methods were 0.004  $\mu\text{g/g}$ ; however, preference was given to direct sample injection, as a simpler, more rapid, and commercially available method.

The introduction of samples into atomic spectrometers as microemulsions (drop size above 5–100 nm) became an alternative to the dilution of oil products with organic solvents. The procedure of the emulsification of viscous oils and their derivatives differs by simplicity, does not require large volumes of organic solvents, reduces matrix effects, and allows the use of

inorganic reference materials for instrument calibration. The formation of microemulsions includes the dissolution of surfactants (emulsion stabilizers) in an aqueous solution followed by mixing with an organic phase under stirring or in an ultrasonic bath within 5–10 min. The results of ETAAS using emulsification depend on the quality of homogenization of the test solution. The determination of stable vanadium compounds in oil products became possible using an emulsion prepared from conc.  $\text{HNO}_3$ , Triton X-100, test sample, and water in the ratio 1 : 1 : 2 : 6, respectively [37]. The emulsion was homogenized on an US setup. The proposed procedure was used to determine vanadium in samples of gasoil, petrol, and diesel fuel. The LOD for vanadium was 14  $\mu\text{g/L}$ . The introduction of samples of crude oil, diesel fuel, and petrol as emulsions with hexane and a solution of Triton X-100 into an ETAAS spectrometer allowed Luz et al. to simultaneously determine trace amounts of Co, Cu, Pb, and Fe [38].

Examples of determination of vanadium in fuel oil by ETAAS with sample introduction into an atomizer by two methods, as a microemulsion and after acid digestion, were described in [39]. In the preparation of an emulsion, a sample of fuel oil was dissolved in xylene to reduce viscosity, conc.  $\text{HNO}_3$  was added, and the mixture was placed in an US bath for 5 min. The solution obtained was vigorously shaken with a water-methyl isobutyl ketone-*n*-propanol mixture within 1 min to obtain a microemulsion. The LOD for vanadium after sample introduction as a microemulsion was of about 0.10  $\mu\text{g/g}$  in comparison to 0.25  $\mu\text{g/g}$  for the use of acid digestion.

In [40] V, Ni, and Co in fuel oil were also determined by introducing a sample-toluene-nitric acid-xylene-Triton X-100-water microemulsion into an atomizer. The limits of detection for V, Ni, and Co were 5.7, 6.5, and 0.07  $\mu\text{g/g}$ , respectively. Examples of the determination of vanadium and nickel in crude oil and oil products using an emulsion xylene-sample-Triton X-100-nitric acid with a modifier (Pd) and without it were described in [31, 41–43].

The injection of samples diluted with organic solvents into an atomizer is most often used, because this method is simple and differs by rapidity, accuracy, and reproducibility. However, the analyzed solutions are unstable in time because of the evaporation of solvents and the adsorption of TEs on container walls; some solvents are toxic; and expensive organometallic reference materials are necessary for the calibration of instruments. The determination of lead in samples of oil condensate in xylene was described in [44]; vanadium was determined in the samples of heavy oil diluted with a mixture of tetrahydrofuran with white oil (1 : 1) using a tungsten-modified graphite furnace [45]; Cd, Cr, Cu, Pb, Ni were determined in samples

of gasoil and petrol diluted with heptene in an transversely heated electrothermal atomizer [46].

**Inductively coupled plasma atomic emission (optical emission) spectrometry.** ICP AES (ICP OES) is a state-of-the-art multielement method of analysis, characterized by high accuracy and productivity, wide dynamic range, and possibility of the direct analysis of complex organic samples, oils among them. However, in working with organic media, the researcher should take into account problems associated with plasma instability and interferences [25, 77], which reduce the sensitivity of ICP AES and casts some doubt on its efficiency in the determination of elements present in samples in very low concentrations. As was shown in [47, 78–82], the analysis of organic samples (including oils) by ICP AES requires special configurations of the system of sample introduction (torches, dispensers, sputtering chambers); optimum values of working parameters of the instrument; availability of an auxiliary gas, oxygen (to minimize interferences and deposits on the surface of instrument units); and calibration of the spectrometer.

To introduce oil products into an atomic emission spectrometer, analysts often use sample dilution with organic solvents or introduction of test samples into the spectrometer as emulsions. The choice of a solvent is one of the most important stages, as the solvent must completely dissolve the sample and form a system stable in time, be nontoxic whenever possible, give stable plasma, and minimize interferences. The determination of vanadium and nickel in oil samples diluted with 1,2-dimethylbenzene was described in [83]; determination of lead in aviation fuel (in toluene), in [47]; determination of V, Ni, and Fe in a number of standard samples (metals in oil products) diluted with tetraline, in [48]; and determination of a wide range of metals in samples of oil from Western Siberia dissolved in xylene was described in [49].

In [50] ICP AES was used to analyze solutions of heavy oil residues (HORs) from Shpakov, Chernigov, and Samara oils in xylene and toluene. It was shown that LODs for elements, such as Mg, Al, Ca, V, Ni, and Zn, in xylene are lower than those using toluene as a solvent. The accuracy of the results of analysis was checked by the method of standard additions using a Conostan S-21 multielement standard solution (Canada) with concentration of each element (Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, Zn as cyclohexane butyrate) in light oil 900 µg/g. Simultaneously TEs were determined in HORs by ICP MS after autoclave decomposition. The results of determination of concentrations of the majority of elements in various HORs by ICP AES with the introduction of a HOR solution in xylene and toluene were comparable with the results of their determination by ICP MS after the autoclave decomposition of HORs. The duration of element determination in a sample diluted with toluene or xylene by

ICP AES, including the sample preparation stage, did not exceed 30 min, whereas the standard method with autoclave decomposition took not at least one hour.

The introduction of samples of oil products as emulsions allows the researchers to improve the sensitivity of the method and also to use inorganic reference materials for the construction of calibration dependences. In [51] samples of crude oil were introduced into an ICP AES spectrometer as an emulsion oil–n-propanol–water–conc. HNO<sub>3</sub> (6 : 70 : 20 : 4, w/w) using a Meinhard nebulizer and the addition of oxygen to plasma. Propanol was used as cosolvent responsible for the homogeneity and stability of the emulsion. The LODs for analytes (Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr, Co) varied from 0.4 to 13 ng/g. Souza with coauthors [52] also demonstrated prospects for the use of two methods of emulsification (in the presence of a surfactant and without it, with the addition of conc. HNO<sub>3</sub>) along with the dilution of samples with organic solvents (kerosene, xylene) for the determination of Mo, Cr, V, and Ti in samples of diesel fuel. A method for the determination of Ba, Ca, Mg, and Na in an oil sample by the formation of an emulsion oil–xylene–5% solution of Triton X-100–10% HNO<sub>3</sub>–water followed by its separation at 80°C was proposed in [53]. Organic and water phases were separated in a centrifuge; and water phase was analyzed by ICP AES. The authors believed that the complete extraction of elements was reached within one cycle.

**Microwave plasma atomic emission spectrometry (MP AES) and laser spark emission spectrometry (LSES).** Today these methods are at the stage of development and have not received wide acceptance in the analysis of oils. The main restrictions of these methods [84, 85] are associated with their insufficient sensitivity and productivity in the determination of TEs. However, Nelson with coauthors in [54] showed a possibility of using MP AES for the determination of V, Ni, Fe, Ca, and Na after the direct introduction of oil sample solutions in xylene. The accuracy of the method was confirmed by comparing the results of analysis of the same samples by ICP MS and ICP AES. The LSES method was proposed by Gondal [55, 56] for the determination of Ca, Fe, Mg, Cu, Zn, Ni, and Mo in residual fractions of Arab oil and 13 elements in asphaltenes. Martínez [57] also analyzed a sample of Venezuelan oil encapsulated in a zirconia xerogel for the presence of nickel and vanadium by LSES.

**Inductively coupled plasma mass spectrometry** is a multielement method of analysis characterized by high sensitivity; taking into account low background, LODs can be of about ng/L and lower. However, the direct determination of TEs in organic media (oil products) by ICP MS is a complex problem and now remains at the level of research. Among the problems arising in the analysis of organic media, most often are plasma quenching or instability, interferences of poly-

atomic compounds, deposits on interface units and ionic lenses, matrix effects, and poor availability and high cost of organometallic reference materials. To solve these problems, as in the case of ICP AES, special sample introduction systems were proposed (US dispensers, microdispensers, cooled sputtering chambers); oxygen gas was used to remove deposits from the surface of spectrometer units; interferences were reduced in reaction cells; etc. [25, 86–88].

The determination of 16 elements in asphaltenes and maltene fractions of Brazilian oil using an ICP MS spectrometer with an US dispenser and the direct introduction of a sample solution in toluene with the addition of oxygen to argon plasma was described in [58]. The accuracy of the results was validated by the analysis of standard NIST samples (metals in lubricant oil, fuel oil) and also by the determination of TEs after the acid digestion of samples. A procedure for the determination of V, Ni, Cu, Mo, Ag, Sn, Ba, Pb, and Cd in samples of crude oil and its fractions, asphaltenes and maltenes, diluted with *o*-xylene using a microdispenser and a cooled sputtering chamber, was presented in [59]. Pohl with coauthors in [60] determined 17 elements in samples of oil diluted with *o*-xylene using double focusing ICP MS. The use of a reaction cell in [61] allowed the researchers to lower LODs for V, Ni, and Mo in samples of oil diluted with *o*-xylene (1 : 10). A comparative analysis of the results of determination of TEs in crude oil and petrol by ICP AES and ICP MS after the direct introduction of samples diluted with *o*-xylene was made presented [62, 63].

The direct determination of TEs in oil products became possible using the ICP MS method in combination with laser ablation or thermal evaporation, in which the analyzed sample did not require sample preparation (decomposition or dilution). Laser ablation (LA) is a process of the interaction of laser radiation with a substance, in which the sample melts, evaporates, or at once sublimates to form of a fine aerosol, which is transported to the area of inductively coupled plasma with a carrier gas flow. In spite of the fact that LA ICP MS was proposed more than 30 years ago, only a small number of papers on the determination of TEs in oils by this method was published by the moment. Among the main shortcomings of the method let us note a rather small number of standard samples with suitable matrices, difficulties with the calibration of instruments, interferences, matrix effects, sputtering in the interaction of a substance with the laser, presence of sample heterogeneity at the ablation point, and in most cases difficulties in ensuring a good reproducibility of the results. However, the authors of works [64–68] proposed a method for the determination of trace amounts of TEs in oil samples by LA ICP MS. An oil sample was placed on a cellulose [64] or silica [65] plate as a zirconium xerogel [66] or put in a glass dish [67]. By selecting the optimum working parameters of the laser, the researchers could

reduce matrix effects and interferences of polyatomic compounds and determine concentrations of TEs at a level ng/g. An example of the determination of 11 elements (Na, Mg, Al, Ti, Cr, Fe, Ni, Co, Cu, Ag, Pb) in lubricant oils by laser ablation and inductively coupled plasma time-of-flight mass spectrometry was described in [68].

A combination of methods of laser ablation and thin-layer chromatography opened a possibility of the development of a method for the determination of the speciation of Ni, Fe, and V in crude oil and its fractions. The concentrations of vanadium and nickel in the sample were 0.023 and 0.018 ng/g, respectively [89].

In ICP MS with electrothermal evaporation, as in ETAAS, the matrix is eliminated before the evaporation of the substance to be determined, which reduces the effect of polyatomic spectral hindrances and the degree of deposition on the units of the spectrometer. In addition, TEs can be preconcentrated by multiply applying sample onto the substrate and drying it in a graphite tube. Thus, concentrations of Cu, Ni, Mn, and Sn in a petrol sample were determined by ICP MS with electrothermal atomization [69]. The test sample was introduced into a graphite tube as an emulsion sample–water–Triton X-100–nitric acid. The limits of detection for Cu, Mn, Ni, and Sn in the sample were 0.22, 0.02, 0.38, and 0.03 µg/L, respectively.

**X-Ray fluorescence (XRF) analysis** because of its limited sensitivity in the determination of TE in oil products often demands the use of various methods of physical and chemical preconcentration [90, 91].

A method of the direct determination of Ca, Fe, Ni, and V in crude oils by XRF was proposed in [70]. Samples of crude oil were homogenized, diluted with toluene (1 : 1), and placed in the center of filter paper pressed between two polypropylene films. A method for the determination of iron and copper in petrols by power dispersive XRF was proposed in [71]. After distillation, a sample residue was put onto a cellulose disk, dried, and covered with a polyethylene terephthalate film. Fe, Cr, Cu, Zn, and Pb in lubricant oils were determined in a wavelength dispersion spectrometer [72]. The determination of vanadium and nickel [73] and also iron [74] in oil samples, bitumens, and asphaltenes was also described.

**Electrochemical stripping methods** also ensure the determination of TE in oil products, but preliminary sample preparation through the decomposition and elimination of the organic matrix are necessary. Thus, after the microwave decomposition of samples of diesel fuel and oil, Cu, Pb, and Hg were determined by stripping voltammetry and chronopotentiometry on gold film electrodes and Cu, Pb, and Zn, by stripping potentiometry on mercury film electrodes [92]. The limits of detection were, correspondingly, 0.063, 0.053, and 0.18 µg/g for Cu, Pb, and Zn in using strip-

ping potentiometry and 98 and 104 ng/g for copper and mercury in using stripping chronopotentiometry.

Stripping potentiometry on a gold film electrode was used to determine copper and lead in lubricant oils after ultrasonic extraction with conc. HCl and hydrogen peroxide [93]. The LODs for lead and copper in the sample were 0.067 and 0.023  $\mu\text{g/g}$ , respectively.

Stripping voltammetry on a hanging mercury drop anode was used for determination of zinc in automobile lubricant oils. Samples were decomposed by ultrasonic extraction in the presence of HCl and  $\text{H}_2\text{O}_2$  on heating ( $90^\circ\text{C}$ ) within one hour. The limit of detection for zinc was 6  $\mu\text{g/g}$  [94].

A method for the determination of lead and cadmium in petrols by stripping voltammetry on a mercury film electrode without preliminary sample decomposition was proposed in [95]. The sample was introduced into the analyzer as an emulsion 0.1 M  $\text{HNO}_3$ -Triton X 100-*n*-butanol-water; the organic phase was petrol. Concentrations of metals were determined simultaneously by two independent methods, XRF and spectrophotometry. The authors believe that, because of the formation of a stable emulsion, the organic components of the matrix were bound and the access of metal ions to the electrode surface was thus improved.

**Other methods.** Neutron activation analysis is a direct method of element determination; however, it requires careful preparation of samples of crude oil and oil fractions [96, 97].

Electron paramagnetic resonance was used for the determination of transition metal complexes, for example, porphyrin complexes of vanadium V, in oil products [98–100]. Studies on the determination of the element speciation of oil and its fractions were performed using a combination of methods of liquid and gas chromatography with spectroscopic methods of analysis [101–105].

#### METHODS OF SAMPLE PREPARATION TO THE INSTRUMENTAL DETERMINATION OF TRACE ELEMENTS IN OIL

Methods of sample preparation, ensuring the extraction of TEs from oils (extraction, sorption, electrochemical, magnetic, ultrasonic, etc.) are being actively developed now. The extracted elements can be determined by any of the available instrumental methods of analysis. The main methods of oil sample preparation are described below.

**Ashing and acid digestion in open and closed systems, microwave and ultrasonic treatment.** In the analysis of oils by ICP AES and ICP MS, the sample preparation stage often involves ashing and acid digestion of samples with the transfer of the components to be determined to the water phase [25–27]. A comparative analysis of the often used methods of oil sample preparation is presented in Table 3.

Sample mineralization is carried out in open or closed vessels (Carius tubes; polytetrafluoroethylene, quartz, or platinum vessels), autoclaves on heating and under elevated pressure, or with US or microwave treatment in the presence of concentrated acids and oxidants [106–119]. However, destructive methods of oil sample preparation have a number of disadvantages: losses of volatile compounds, work with poorly representative samples (limited sample mass in using pressure, sample dilution and impossibility of TE pre-concentration), and pollution and incomplete decomposition of the organic matrix.

A combination of the acid digestion of samples with ultrasonic treatment was proposed in [111] for the determination of Cr, Mo, Ti, V, Cd, Fe, Mn, Ni, and Zn in crude oils. Crude oils were treated with conc.  $\text{HNO}_3$  and heated to  $85^\circ\text{C}$  within 30 min. Then solution was placed in an ultrasonic bath for 15 min for the complete extraction of TEs from the sample to the acid solution.

The use of autoclaves (including those with microwave treatment) for the decomposition of samples of oil origin ensures the almost complete removal of the organic phase at one stage. This method is rather fast (takes less than 1 h) and provides a convenient destructive method of the closed type (allows work with acids of different types under pressures up to  $10^7$  Pa and temperatures up to  $350^\circ\text{C}$ ) [112–115]. In [113], crude oil was decomposed in quartz vessels in a microwave oven (in the presence of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}_2$ ) under severe conditions:  $300^\circ\text{C}$  and  $1.216 \times 10^7$  Pa; 63 elements were determined. Using the acid digestion of oils and HORs in an autoclave in the presence of chloric and nitric acids on heating and at elevated pressure ( $350^\circ\text{C}$ ,  $1.8 \times 10^6$  Pa), Gottikh et al. could determine a wide range of TEs by the ICP MS [114, 115].

The application of the microwave ashing of oils in a closed system to the subsequent ICP MS determination of the concentration of REE was described in [116–119]. Oil samples in polyethylene films or polycarbonate capsules were placed in quartz vessels filled with 2–3 M  $\text{HNO}_3$  (absorbing solution, in some cases with an addition of hydrogen peroxide), and subjected to ashing in the presence of oxygen ( $2 \times 10^6$  Pa) and 50  $\mu\text{L}$  of 6 M  $\text{NH}_4\text{NO}_3$  (igniter) in a microwave setup according to the proposed program. The results of ICP MS analysis of samples prepared by microwave ashing were comparable with the results of ICP MS determination using acid digestion in a closed system with microwave irradiation. In addition, the use of microwave ashing allowed the reduction of LODs for a number of elements by one order of magnitude in comparison with the method of acid digestion in a closed system using microwave irradiation.

**Extraction methods.** Among the important advantages of extraction methods of sample preparation are versatility to the nature of extracted elements and their

**Table 3.** Comparative characteristics of methods for sample preparation of oils

Method of sample preparation	Sample weight	Advantages	Disadvantages	Percentage of publications in 2002–2012 [26]
Ashing in flame	Up to 100 g	Simplicity of procedure, work with representative samples	Losses of volatile compounds of many metals, long sample preparation	8
Direct introduction/ dilution		Exclusion of analyte losses, simplicity, initial chemical composition of the sample do not change	Necessity of instrument modernization, high blank values, insufficient values of LOD	Direct introduction – 14; as emulsion – 9; dissolution in organic solvents – 24
Acid digestion	Up to 100 g	Work with representative samples	Limited number of acids, losses of volatile compounds, incomplete decomposition of organic matrix	34
Autoclave decomposition	Up to 1 g	Transfer of the majority of trace impurities into solution in one cycle	Explosion hazard, small sample weighed portions, incomplete dissolution, possibility of introduction impurities of autoclave materials	
Microwave decomposition	Up to 1 g	Transfer of the majority of trace impurities into solution in one cycle	Small sample weighed portions, possibility of incomplete dissolution, losses of volatile compounds	
Extraction	–	Simplicity and low cost of analysis, variety of extractants, possibility of preconcentration in the versions of RCC and SPE	Dependence of element recovery on their speciation in oils	5
Other methods				6

concentration, simplicity, and rapidity. Extraction methods of sample preparation offer a possibility of the determination of not only the total concentration of TEs, but also their speciation in oil raw materials, which is important for the study of the genesis of oils and environmental monitoring. Elements are extracted from oils with mineral acids, alkalis, oxides, and organic reagents. As was stated above, the majority of TEs significant for petrochemistry occur as porphyrin and nonporphyrin complexes. The most part of studies on extraction methods of sample preparation were devoted to the extraction and study of porphyrin complexes of elements from oil raw materials, in particular, from asphaltene and pitch fractions. The ratio of the types of metal porphyrins gives important information for the determination of the nature, age, and source of oil. An example of the extraction of porphyrin complexes of vanadium and nickel from pitches and asphaltene of oil of the Zyuzevskoe field by concentrated acids, sulfuric, nitric, orthophosphoric, and a mixture of sulfuric and nitric acids (2 : 1) was described in [120]. The total concentration of elements in oil, asphaltenes, and pitches was determined by flame AAS. A solution of asphaltene (pitch) in carbon tetrachloride was mixed with acids, the extract was separated by centrifugation followed by filtering through a funnel with a glass filter. Then the acid extract was neutralized with a sodium hydroxide solution, and free metal porphyrins were extracted with carbon tetrachloride and determined by spectrophotometry. Types of metal porphyrins were determined by their separation on a chromatography column with a 0.5% solution of isopropanol in benzene. The yield of vanadyl porphyrins was no more than 60% of their total concentration in asphaltenes and 100% for pitches.

A method was described for the extraction of metal porphyrins from asphaltene solutions with concentrated acids (sulfuric and phosphoric) at room temperature [121, 122]. It is known that  $\text{TiCl}_4$  and  $\text{SnCl}_4$  form insoluble complexes with metal porphyrins in hydrocarbon raw materials. Samples of oil and oil fractions were dissolved in hexene in the ratio 1 : 2 and treated with different volumes of a 10% solution of titanium (tin) tetrachloride in the hexene. The precipitate obtained was separated by centrifugation, dissolved in water, and metal porphyrins were extracted with chloroform. Vanadyl porphyrin was determined by spectrophotometry. The authors noted that they achieved the complete extraction of vanadyl porphyrin from the analyzed solution [123].

A chemical method of metal extraction from oils with the decomposition of their organic compounds by acids and oxides was described in [124]. Vanadium and nickel were extracted from HORs on heating (250°C within 30 min) using solutions of sulfuric, phosphoric, hydrofluoric, acetic, maleic, and citric acids; heptane, toluene, tetrahydrofuran (THF), and dimethylformamide (DMFA). 82% of vanadium and

88% of nickel were extracted from oil with sulfuric acid; however, in the course of extraction the formation of a stable emulsion and a change of the color of oil because of the formation of oxidation products were observed. The authors believed that the best results in the extraction of metals from organic compounds without a change of the physical and chemical properties of oil were obtained using 5% maleic acid in DMFA. In [124], extractants were also solutions of inorganic salts, sodium and magnesium sulfates, and iron and tin chlorides. A reagent with a sample was mixed in different ratios, the mixture was heated to 200°C within 30 min, and the upper layer of the organic phase was analyzed. The recoveries of vanadium and nickel from heavy oil with a 0.5 M  $\text{FeCl}_3$  solution were 40 and 22%, respectively.

The organic solvents for the extraction of metal porphyrins from oil and oil products are often ethanol, acetone [125, 126], methanol, acetonitrile [102], DMFA [121, 127], mixtures based on pyridine [101, 104, 105], etc.

According to patent [128], ethylene carbonate as an extractant extracted up to 93% of vanadium and 89% of nickel from oils and its residues. Extraction was carried out in the countercurrent mode at the ratio extractant : oil product lower than 0.1 : 1 on heating from 80 to 200°C; the concentration of metals was determined by spectrophotometry in UV and visible spectral regions.

The efficiency of using various extractants for the extraction of nickel and vanadium from oil was studied in [129]. The complete extraction of these metals was attained using DMFA in a mixture with maleic or benzoic acids. Metals were determined by spectrophotometry in the UV spectral region.

As was shown in [130], the addition of 2-propanol in combination with photoirradiation within 36 h weakens bonds between metal porphyrins and asphaltene components of oil, because of which the recovery of metal porphyrins from oil and oil products can be increased. Thus, after the distillation of 2-propanol, 1 M HCl extracted about 93% of vanadium and 98% of nickel from the residue of atmospheric distillation and 73% of vanadium and 85% of nickel from the residue of vacuum distillation. The concentration of metals in the extracts was determined by ICP AES.

Galimov et al. in patent [131] proposed the use of 5–30% alcohol (C3–C4) or acetone solutions of mono- or bifunctional carbonyl compound, such as diacetone alcohol, methyl ethyl ketone or acetoacetic ester, acetylacetone, for the extraction of vanadyl porphyrin from pitches and asphaltenes.

The application of rotating coiled columns (RCCs) opened a possibility to develop a new method for the extraction and preconcentration of TEs from crude oil and THOs [132–134]. Rotating coiled columns are tubes (Teflon capillaries) wound around a rigid or a flexible core as single-layer or multilayered coils. One

of phases (stationary), an aqueous solution of inorganic acids or an organic extractant, is retained in the RCC without using a solid support or an adsorbent because of the effect of the field of mass forces, arising in the column rotation about its axis and its simultaneous revolution around the central axis of the instrument (planetary centrifuge). The second phase of the system (mobile), oil or oil products, is simultaneously pumped through the stationary phase. The use of RCCs allows the analyst to implement multistep extraction and extract analytes without changes in the physical and chemical properties of oil. It was shown that use of RCCs offers a possibility of working with a wide range of oil products and extraction systems. In addition, RCCs ensure not only extraction but also preconcentration of trace elements from oil in a rather small volume of a stationary phase.

Supercritical Fluid Extraction (SFE) is a rather new technological process, based on unique properties of solvents in the supercritical state. Supercritical solvents possess high diffusion coefficients and low surface tension and viscosity. Their solvent power can be varied in the wide range by changing pressure and temperature. Fluids differ in the simplicity of their separation from dissolved substances on reducing pressure [135]. The most widely used fluids are carbon dioxide, propane, and water. The use of carbon dioxide is often most preferable because of its low cost, nontoxicity, and suitable parameters of the critical state [136].

The effects of pressure, temperature, and time on the extraction of elements from metal porphyrins was studied by SFE in [137, 138]. Elements were extracted under the following conditions: 410–490°C, pressure  $2.5 \times 10^7$ – $4.5 \times 10^7$  Pa, duration 60–180 min in the presence of supercritical water and toluene. At 450°C and pressure growth from  $2.5 \times 10^7$  to  $4.5 \times 10^7$  Pa, the amount of extracted nickel porphyrins increased from 60.04 to 76.41% and, in terms of pure nickel, from 46.89 to 54.77%. A number of vanadyl porphyrin remained insoluble under these conditions. With an increase in time of extraction to 180 min and temperature to 490°C, the recovery of elements considerably increased to 80.26% for vanadium and 76.41% for nickel. The concentrations of metals in the extract were determined by flame AAS.

**Membrane filtration.** Now membrane filtration is used for the extraction of asphaltenes, containing the most part of TEs, from oil products, including heavy oils.

The results of extraction of asphaltenes from samples of Iranian oil on asymmetric monolithic ceramic membranes of the size from 0.2  $\mu\text{m}$  to 50 nm on heating from 79 to 190°C at a pressure difference of  $2 \times 10^5$  Pa and the subsequent determination of the concentrations of V, Ni, Na, and Fe in the extract were reported in [139, 140]. The recovery of organometallic compounds from oil attained a maximum using mem-

branes with the minimum pores. The concentration of elements was determined by AAS, the recoveries of vanadium and nickel were 63–83 and 25–52% for three samples of oil, respectively. Monolithic ceramic membranes with pore diameter of 0.1–1.4  $\mu\text{m}$  heated to 190°C were used for the ultrafiltration of heavy oils [141].

A possibility of application of the ultrafiltration heavy oils to the extraction of asphaltenes containing organometallic compounds by single tube ceramic membranes with pore diameter of 0.02–0.1  $\mu\text{m}$  at 110°C and pressure gradient of  $6 \times 10^5$  Pa was shown in [142]. The concentration of vanadium in an oil sample after ultrafiltration was reduced from 190 to 61  $\mu\text{g/g}$  and that of nickel, from 76 to 27  $\mu\text{g/g}$ . The concentration of vanadium was determined by the direct introduction of test samples in xylene into an ICP AES spectrometer.

A possibility of the filtration of oil products at 200–300°C and pressure gradient  $4 \times 10^5$  Pa using ceramic membranes with pore diameter 0.02–3  $\mu\text{m}$  was shown in [143]. The recovery of metals from oil was up to 45% for nickel and 41% for vanadium. Ceramic membranes, in contrast to polymeric ones, allow the use of high temperatures and pressures and aggressive solvents within a rather long time. In addition, the use of high temperatures favors the clusterization of asphaltene with bound organic metal compounds of bigger size; the efficiency of extraction correspondingly increases. However, one of disadvantages of membrane methods is the contamination and pollution of membrane pores and the reduction of the flow rate of sample solution in the course of filtration.

**Electrochemical methods.** An innovative electrochemical method of the individual extraction of TEs from oil was described in [144]. Crude oil was treated in a flow under the action of alternating asymmetric current of the density 50–100  $\text{A m}^{-2}$  with asymmetry 8–10 and frequency, depending on the atomic weight of the extracted element and its oxidation state. V, Ni, and Fe were extracted from oil in three two-chamber diaphragm electrolyzers (according to the number of extracted elements) by passing one liter of crude oil through flow anode chambers at a rate of 1.389 mL/s. Cathodic static chambers contained 50 mL of a receiving 0.01% aqueous buffer solution of HCl. The recoveries of V, Ni, and Fe were 90–98%. The proposed method can be used for the determination of element concentrations in oil and oil products.

In [145] vanadium and nickel were extracted from crude oil and HORs by electrolysis in the system test sample–0.2 M  $\text{LiClO}_4$  solution–THF with an addition of a protonating agent, alcohol (methanol). Electrolysis was carried out at a current density of 100–200  $\text{A m}^{-2}$  at a lead cathode. At the last stage, benzene was added to extract metal porphyrins. After the distillation of benzene, the concentration of TEs in

the product was determined by XRF. The recoveries of vanadium and nickel from oil were 35 and 31% and those of HOR, 81 and 87%, respectively. Welter with coauthors in [146] extracted metals from standard porphyrin complexes and their extracts from crude oil and also extracted V, Ni, and Fe directly from crude oil by cyclic voltammetry on glassy carbon, graphite, and platinum cathodes. The surface of the working electrode after electrolysis was analyzed for the concentration of metals by ICP AES and XRF. The maximum recovery of metals (84%) was attained for commercial porphyrinates (glassy carbon cathode, 2.3 V, THF–metanol–HClO<sub>4</sub>). The recovery of TEs from extracts of porphyrin complexes of oil was 66.44% on the graphite cathode; at the direct electrolysis of crude oil, recoveries were only 7.5% for V, 8.2% for Ni, and 79.6% for Fe.

**Sorption methods.** The adsorption of nickel and vanadium from crude oil on a NH<sub>4</sub>Cl-modified clay was studied in [147]. The recovery of metals from crude oil at 25°C, pH 4.8, and time of contact 720 min on the addition of 0.8 g of the adsorbent to 50 mL of oil was 97.6 and 98.6% for nickel and vanadium, respectively.

A possibility of using synthetic zeolites (zeolite A: Na<sub>46</sub>[Al<sub>54</sub>Si<sub>146</sub>O<sub>384</sub>] · 24H<sub>2</sub>O; zeolite Y: Na<sub>56</sub>[Al<sub>56</sub>Si<sub>136</sub>O<sub>384</sub>] · 250H<sub>2</sub>O; zeolite K-L: K<sub>6</sub>Na<sub>3</sub>[Al<sub>9</sub>Si<sub>27</sub>O<sub>72</sub>] · 21H<sub>2</sub>O) for the selective extraction of Ni, V, and S from crude oil was studied in [148]. In the experiment, a zeolite powder was dispersed in 50 mL of crude oil and 25 mL of an aqueous solution of an EDTA salt was added to the mixture. The mixture was carefully stirred within 1 h at 18°C and allowed to stay for 24 h before complete phase separation. The extracted water phase was analyzed by ICP AES.

It was shown in [149] that the ionic polymeric adsorbent based on magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles is an effective material for the selective extraction and preconcentration of vanadium(IV) from crude oils. The adsorbent was obtained by the copolymerization 3-(triethoxysilyl)propyl methacrylate (monomer), ethylene glycol dimethacrylate (sewing agent), and a vanadium(IV) complex of 1-(2-pyridylazo)-2-naphthol. A sample of oil was mixed with a solution of Triton X-100 in nitric acid and then the emulsion formed was broken by heating to 80°C. The water phase containing the extracted metals was separated and an adsorbent was added to the solution formed. The adsorption process took 3 min, the adsorbent was separated in a magnetic field, and vanadium(IV) ions were removed from the adsorbent with a solution containing thiourea and HCl. The concentration of vanadium in the obtained solution was determined by ETAAS. About 97.6% of vanadium was extracted by this method from oil samples.

\* \* \*

Technical modernization of instruments and the development of new efficient methods of direct introduction (microemulsification, laser ablation, electrothermal evaporation) ensured the improvement of the sensitivity and productivity of state-of-the-art methods of oil analysis (ETAAS, ICP MS, ICP AES (ICP OES), stripping electrochemical methods). Sample preparation of oils is performed by traditional methods of ashing and acid digestion (in closed and open systems) and also by extraction, electrochemical, membrane, and sorption methods. In recent years, methods of oil sample preparation by the extraction of TEs, filtration on monolithic ceramic membranes with nanopores, and sorption extraction on nanoparticles have been actively developed.

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