geosciences

MDPI

Article

Trace Metal Contents of NIST 1634c and NIST 8505 Multi-Element Petroleum Reference Materials: Compilation of Published Data and New Results Evaluating Acid Digestion Procedures

Emiliya Raeva *, Lora Bidzhova, Gatien Morin and Svetoslav Georgiev

Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
* Correspondence: emiliya@geology.bas.bg

Abstract

Knowledge of the trace element contents of petroleum can improve crude oil exploration and refining and aid environmental studies. Analytical challenges prompt experimentation with various digestion methods and analytical techniques, but the assessment of the efficiency of applied methodologies is hindered by the scarcity of multi-element standard reference materials. In this study, NIST SRM 1634c residual fuel oil and NIST RM 8505 crude oil were subjected to (i) hotplate acid digestion and (ii) one, two or three cycles of microwave acid digestion, and analyzed by ICP-MS. Comparison with the few available certificate values shows optimum recoveries for both reference materials with two and three cycles of microwave digestion. Hotplate digestion can also efficiently decompose petroleum, although this procedure requires more time and reagents than the microwave digestion. To better characterize the trace element composition of the two reference materials for future use in the community, we integrate our new results with a comprehensive compilation of published trace element data for both petroleum samples. Finally, we show that the V/Ni and V/(V + Ni) ratios commonly used for oil–oil and oil–source rock correlations remain sufficiently close to the expected ratios even in cases of incomplete digestion with lower recoveries for both elements.

Keywords: microwave digestion; ICP-MS; trace elements; compilation; V/Ni ratios

1. Introduction

Crude oil and natural petroleum products such as condensate, bitumen, asphalts, tar and others are complex mixtures of various hydrocarbons, some amounts of water, and possibly entrained minerals. As such, their elemental composition is dominated by C and H (~94 to 100%), with smaller amounts of N, O, and S (~1% to 6%). In addition, they also contain trace amounts of various elements, primarily metals (e.g., V, Ni, Mg, Al, Fe, Ba, As, Mn, Cu, etc.), many of which were transferred from seawater into sedimentary organic matter, and upon thermal maturation, ultimately into newly generated petroleum [1,2]. Additionally, trace metals (TMs) are either added or removed from crude oil after generation during secondary processes. Therefore, trace metal abundances and their ratios can provide insight into the complex processes forming petroleum systems, such as the deposition of organic-rich rocks, maturation of organic matter, crude oil generation and migration, and biodegradation. For example, trace metal contents and ratios in crude oils are widely used for oil-to-oil and oil-to-source rock correlations (e.g., [3–6]). Their application is

Check for updates

Academic Editor: Mirko Severi

Received: 16 December 2025
Revised: 30 January 2026
Accepted: 4 February 2026
Published: 8 February 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license.

particularly valuable for biodegraded petroleum products that lack the organic biomarker molecules commonly used for correlation purposes. Among the trace metals, the most widely used for genetic correlations are V, Ni, Re, and Os. Vanadium and Ni are often studied due to their relatively elevated abundances (sometimes exceeding 1000 μg mL^{-1}), well-understood controls on their incorporation in sedimentary organic matter and crude oil, and usually constant weight ratios in genetically related sedimentary organic matter, kerogens, crude oil, and biodegraded oil (e.g., [3,5]). During sediment formation, both metals are transferred from the water column into sedimentary organic matter and are hosted there primarily in porphyrin complexes derived from chlorophyll precursors and in high-molecular-weight organics. The interplay between geologic factors (e.g., lacustrine versus marine sedimentation, clastic versus carbonate sedimentation), redox potential and pH dictates the proportion of V and Ni entering the organic matter. Vanadium precipitation, for example, is favored by reducing conditions in the water column or sediment pore waters, whereas basic conditions hinder V transfer into organic matter. On the other hand, Ni ions are readily available to bond with organic matter in lacustrine settings lacking sulfate ions, whereas in typical marine sediments, significant activity of sulfate-reducing bacteria provides sulfide ions that bind Ni in sulfide minerals. As a result, lacustrine sediments have relatively high Ni, low V, and low S, and characteristically low V/Ni ratios, and these characteristics are transferred into petroleum derived from such lacustrine organic-rich rocks. As another example, the ample reactive iron during deposition and early diagenesis of clayey source rocks binds most of the available sulfur in marine shales in the form of pyrite, so their organic matter and the petroleum produced by it are relatively sulfur-poor. In contrast, carbonate source rocks are typically S-rich, because the reactive iron is not available during sedimentation, and most of the sulfur binds to the sedimentary organic matter, which can later produce S-rich crude oils. As a result of these geochemical controls, petroleum produced in different geological settings have characteristic V-Ni-S signature that can be used to infer the origin of a given crude oil, genetically distinguish between crude oils, and to correlate them with their source rock (e.g., [3–5,7,8]).

Rhenium and Os contents in crude oils are much lower (usually ng mL^{-1} to pg mL^{-1}) compared with V and Ni. Despite these low concentrations, many studies focus on the radioactive decay of ^{187}Re to ^{187}Os, which offers a radiometric clock for dating the deposition of the source rocks and petroleum generation, and to conclusively link various components of the petroleum system to track their evolution in time using the $^{187}Os/^{188}Os$ isotopic ratios (e.g., [7,9,10]).

Understanding the trace element distribution in crude oil and petroleum products is also important for environmental studies. Natural petroleum seeps and anthropogenic petroleum spills, as well as atmospheric emissions from fuel oil combustion, can release harmful organic compounds and heavy metals to the atmosphere, water, and soils, and thus require regulation and monitoring (e.g., [11]). Trace metals in crude oil, such as V, Ni, Fe, and Mg and their ratios V/Ni, V/Mg or V/(Ni + Fe + Mg), as well as S, N, Co, Cu, and Mn, are known as unique, weathering-resistant fingerprints and have been used to track the source of pollution or to estimate the areal degree of pollution from a known source [12–14]. These trace metal markers (Ni, V, Co, Mn, Mg, Fe, Cr, and Cu as well as V/Ni, V/(V + Ni), and Co/Ni) in crude oil have been utilized in environmental forensics to resolve issues related to identifying the source of rogue spills from tankers or pipelines (e.g., [15]) and spilled petroleum remnants (e.g., tar balls, asphaltites; [16–18]). In addition, elements such as Fe, Na, As, Se, Cd, Pb, and V and Ni in particular, as well as S and N, have harmful effects on the fuel refining process, generally acting as catalyst poisons (e.g., [19–21]); Hg, Na, Cu, As, Ni and V can also be highly corrosive to the refining equipment (e.g., [19–22]).

Despite the importance of trace metal studies in petroleum for petroleum exploration, for optimizing the refining process, and for tracking and minimizing environmental risks, the acquisition of accurate and precise trace metal data in petroleum is hampered by several challenges. Petroleum has an organic matrix and most trace metals are present in low amounts (sub-ng mL^{-1} to single μg mL^{-1} levels), yet some elements like S and V can reach much higher concentrations (5–6 wt% and 0.1–0.2 wt% respectively). The complexity of the organic matrix may present problems during commonly used analytical techniques such as ICP-MS, and thus compromise the quality of the results. Acid digestion is required prior to ICP-analyses to convert the organometallic compounds into inorganic ones, eliminating the negative effects of direct introduction of organic compounds into the ICP instrument [23]. The matrix issue is further exacerbated when the samples are not fully digested, a problem that cannot be easily identified prior to analysis. Analytical techniques that do not require heavy sample pretreatment, such as XRF (X-ray fluorescence) and AAS (atomic absorption spectrometry) (e.g., [24,25]) are not affected. However, these methods generally have inferior sensitivity compared with ICP-MS analyses and, therefore, are not ideal for analyzing multiple TE in petroleum, which are often in the sub-ng mL^{-1} to single-ng mL^{-1} range. An alternative solution is introducing the crude oil sample into an ICP (AES, OES or MS) directly as a solution diluted in organic solvent such as xylene or toluene (e.g., [26], or by emulsifying it in water and surfactants (e.g., [27]). The direct-introduction method is faster, but there are sensitivity issues related to the high dilution factor. In addition, the heavy organic loads can cause plasma instability, carbon deposition and clogging, ultimately resulting in a limited suite of successfully analyzed elements [22,28,29].

ICP-OES and especially ICP-MS instruments (and rarely, the sequential use of both; e.g., [29]), due to their sensitivity and wide operational range in terms of concentrations, remain a preferred choice of instrumentation for analyses of multiple trace metals in petroleum, following appropriate sample preparation either by sample combustion or by acid digestion prior to analysis. A commonly used combustion method is dry ashing in a muffle furnace with sample decomposition in open vessels, as well as closed-vessel combustion in Parr bombs and Schöniger flasks. Advantages of the combustion methods include larger sample amounts (1–20 g) that can improve detection limits. However, the low throughput and higher probability for sample contamination and elemental losses during the combustion makes this a successful application for only a selected group of elements, such as Cl, S, and Rare Earth Elements (REEs) (by combustion bombs and oxygen flask), as well as Cu, Fe, Ni, V, and REEs (by dry ashing) (e.g., [29–33]). As a result, even though acid digestion of crude oils can be time- and reagent-consuming, it is the most widely applied sample preparation method for trace metal analyses of petroleum. On the other hand, complete acid digestion of entirely organic samples is not trivial (e.g., [9]). A variety of digestion techniques for crude oil samples have been employed, including benchtop-hotplate digestion in closed or open vessels, microwave-assisted digestion, microwave-induced combustion, or other closed-vessel acid digestion techniques such as a high-pressure asher or within Parr bombs. These techniques are characterized by various durations, limitations on sample size, exposures to possible contaminants, needs for consumables, and safety protocols. In all of them, the level of sample digestion (complete or incomplete) is usually identified post-analysis, by cross-checking results for certified matrix-matched reference standards run with the samples. However, few such matrix-matched reference materials are available for petroleum, the most commonly analyzed being NIST 1634c (commercial "No. 6" residual fuel oil) and NIST 8505 (Venezuelan crude oil containing visible amounts of water). NIST 1634c is certified for three trace elements (V, Ni and Co); two elements have reference values (As, Se); and

four elements are given as information values (Ba, Cl, Na, S). NIST 8505 provides only one recommended value—for V. As a result, the community lacks a properly characterized multi-element trace element standard for crude oil and trace metal results are often reported with limited or no information on the digestion efficiency and related accuracy of the data. Other multi-element reference materials exist that have a fuller range of elements (e.g., EnviroMAT SCP Science multi-element standard), but these are doped standards and, hence, are less ideal than natural SRMs; they are less frequently analyzed and reported (e.g., [7]).

To address the scarcity of detailed knowledge on the acid digestion efficiency of petroleum products as a critical preparation step for multi-element analysis by ICP, here we present results from several acid digestion procedures and the subsequent ICP-MS trace element measurements of the two most commonly used matrix-matched standards: NIST SRM 1634c and NIST RM 8505. By varying either the heat source (hotplate vs. microwave), sample size, digestion duration, number of digestion cycles or reagent amounts, we study the control of these parameters to determine the most reliable procedures for petroleum digestion. In addition, we combine these results with a newly presented compilation of published data for NIST 1634c and NIST 8505, aiming to better characterize the trace metal content of these materials and thus aid future trace metal studies on petroleum. Finally, we explore the effects of incomplete digestion on key trace metal ratios used in petroleum geology for genetic correlations between crude oils and source rocks.

2. Materials and Methods

2.1. Samples

The objects of our study are two petroleum materials from the National Institute of Standards and Technology (NIST, Gaithersburg, Maryland, U.S.): (1) standard reference material (SRM) NIST 1634c—residual fuel oil—and (2) research material (RM) NIST 8505—Venezuelan crude oil. NIST 1634c is of unspecified geological origin and is likely related to siliciclastic rocks [34]. The geological context for NIST 8505 is also unspecified, but it is probably related to Cretaceous carbonate rocks [34]. Trace metal and Re-Os isotope data additionally constrain its origin to the Maracaibo field with a likely source rock similar to the La Luna Formation, and date the petroleum generation at ca. 79 Ma [7]. This petroleum sample, with a measured density of 986 kg m^{-3} and a calculated API gravity of ~12, is also characterized for major elements (85.4 wt% C; 10.8 wt% H; 2.97 wt% S; 0.41 wt% N; and 0.93 wt% O) [7]. Both NIST 1634c and NIST 8505 are commonly used as a verification tool for the level of petroleum decomposition and the reliability of the analytical results in petroleum studies (Table 1).

Table 1. List of publications reporting trace metal data for NIST 1634c and NIST 8505.

Ref. #	Author, Year	Sample Preparation Method	Analytical Instrument	*n* (A)
		NIST SRM 1634c		
[35]	Nelson et al. 2016	Direct introduction by dilution	MP-AES	2
[36]	Poirier et al. 2017	Direct introduction by dilution	MP-AES	2
[37]	Poirier et al. 2018	Direct introduction by dilution	MP-AES	2
[22]	Hwang et al. 2005	Direct introduction by dilution, MD, HPA-S	ICP-AES-CID	3
[38]	Nelson et al. 2019	Direct introduction by dilution	ICP-OES	2
[39]	De Souza et al. 2011	Direct introduction by dilution	ICP-OES-MFN	2
[40]	Poirier et al. 2016	Direct introduction by dilution	ICP-OES, ICP-MS	2
[41]	Nelson and McCurdy 2017	Direct introduction by dilution	ICP-MS	4
[23]	Dreyfus et al. 2005	Direct introduction by dilution	ICP-MS-MFN	2
[42]	De Souza et al. 2012	Direct introduction by dilution	DRC-ICP-MS	2

Table 1. *Cont.*

Ref. #	Author, Year	Sample Preparation Method	Analytical Instrument	*n* (A)
		NIST SRM 1634c		
[43]	Surekar et al. 2020	Direct introduction by dilution	DRC-ICP-MS	6
[26]	Albuquerque et al. 2012	Direct introduction by dilution, MD	DRC-ICP-MS	2
[44]	Carbonell et al. 2025	Direct introduction by dilution	hTISIS-ICP-MS	1
[45]	Martínez et al. 2024	Direct introduction by dilution	hTISIS-ICP-MS	1
[46]	Pohl et al. 2010	Direct introduction by dilution	SF-ICP-MS	18
[47]	Gajdosechova et al. 2019	Direct introduction by dilution	HS-GC-MS	1
[48]	Tittarelli et al. 2005	Direct introduction by dilution, MD	ET-AAS, ICP-MS	6
[49]	Kowalewska 2013	Direct introduction by dilution	GF-AAS	1
[24]	Doyle et al. 2015	Direct introduction by dilution	ED-XRF	5
[50]	Duyck et al. 2008	Direct introduction by dissolution, MD	ICP-MS-USN	3
[51]	Duyck et al. 2002	Direct introduction by dissolution	ICP-MS-USN	3
[52]	Meervali and Kumar 2001	Direct introduction by emulsion/dilution	TH-ET-AAS, ICP-MS	2
[27]	Lepri et al. 2006	Direct introduction by emulsion	HR-CS GF-AAS	1
[53]	Oliveira et al. 2018	Direct introduction by emulsion	HR-CS GF-AAS	1
[54]	Quadros et al. 2010	Direct introduction by emulsion	HR-CS GF-AAS	2
[55]	Carballo-Paradelo et al. 2009	Direct introduction by emulsion	ET-AAS	3
[25]	Damin et al. 2005	Direct introduction by emulsion	GF-AAS	2
[56]	Luz et al. 2013	Direct introduction by emulsion	GF-AAS	4
[57]	Amorim et al. 2007	Direct introduction by microemulsion, HPD	GF-AAS	1
[58]	De Souza et al. 2006	Direct detergentless microemultion	ICP-OES	3
[59]	Vieira et al. 2019	Direct introduction by nanoemulsion	ICP-OES	1
[60]	Seeger et al. 2018	Direct introduction *in natura*	GF-AAS	1
[61]	Seeger et al. 2019	Direct introduction *in natura*	GF-AAS	2
[62]	Brandao et al. 2007	Direct solid sample analysis	ET-AAS	3
[63]	Polidorio et al. 2008	Direct solid sample analysis	GF-AAS	1
[64]	Silva et al. 2007	Direct solid sample analysis	GF-AAS	2
[65]	Brandao et al. 2006	Direct solid sample analysis	GF-AAS	1
[66]	Dittert et al. 2009	Direct solid sample analysis	HR-CS GF-AAS	2
[67]	DiMarzio et al. 2018	HPA-S	ICP-MS	20
[68]	Cussen and Hensman 2011	HPA-S	ICP-MS, HG/CV-AFS	20
[69]	Ricard et al. 2011	HPA-S	LA-ICP-MS	6
[70]	Walkner et al. 2017	HPA-S	QQQ-ICP-MS	25
[8]	Hurtig et al. 2020	HPA-S	ICP-MS	2
[30]	Wondimu and Goessler 2000	HPA-S, MD	ICP-MS	28
[71]	Ortega et al. 2013	HPA-S, MD, MIC	ICP-MS	5
[72]	Pereira et al. 2010	MIC	ICP-OES, ICP-MS	5
[73]	De Azevedo Mello et al. 2009	MIC	ICP-OES	3
[74]	Pereira et al. 2009	MIC	ICP-OES	2
[75]	Dos Anjos et al. 2018	MD	ICP-OES	2
[76]	Nascimento et al. 2011	MD	AV-ICP-OES	14
[77]	De Almeida et al. 2009	MD	FI-HG ICP-MS	1
[28]	Casey et al. 2016	SRC-MD	ICP-OES, QQQ-ICP-MS	8
[78]	CEM Corporation 2017	MD	ICP-MS	3
[79]	Duyck et al. 2023	MD	ICP-MS	4
[34]	Ventura et al. 2015	MD	ICP-MS	8
[80]	Heilmann et al. 2009	MD and isotope dilution	(LA-)ICP-MS	4
[81]	Henn et al. 2021	MD-PDC	SF-ICP-MS	3
[82]	Trevelin et al. 2016	Extraction induced by emulsion breaking	ICP-OES	2
[83]	Antes et al. 2011	Pyrohydrolysis	DRC-ICP-MS, IC	1
		NIST RM 8505		
[84]	Brenner and Dorfman 1995	Direct introduction by dilution	ICP-AES	1
[85]	Nadkarni et al. 2011	Direct introduction by dilution	ICP-AES	16
[86]	Brenner et al. 2010	Direct introduction by dilution	ICP-OES	1
[38]	Nelson et al. 2019	Direct introduction by dilution	ICP-OES	1
[36]	Poirier et al. 2017	Direct introduction by dilution, Wet ashing	ICP-OES, MP-AES	7
[37]	Poirier et al. 2018	Direct introduction by dilution, Wet ashing	ICP-OES, MP-AES	3

Table 1. *Cont.*

Ref. #	Author, Year	Sample Preparation Method	Analytical Instrument	*n* (A)
		NIST RM 8505		
[87]	Silva et al. 2019	Direct introduction by dilution	ICP-MS	2
[88]	Nelson et al. 2020	Direct introduction by dilution, Iron oxide nanoparticle synthesis	(sp)ICP-MS	1
[25]	Damin et al. 2005	Direct introduction by emulsion	GF-AAS	1
[27]	Lepri et al. 2006	Direct introduction by emulsion	HR-CS GF-AAS	1
[89]	Liu and Selby 2018	Carius tube acid digestion	N-TIMS, MC-ICP-MS	2
[90]	Wang et al. 2022	Carius tube acid digestion	N-TIMS, MC-ICP-MS	6
[67]	DiMarzio et al. 2018	HPA-S	ICP-MS	2
[8]	Hurtig et al. 2020	HPA-S	ICP-MS	16
[7]	Georgiev et al. 2016	HPA-S	ICP-MS, ICP-AES	6
[91]	Sen and Peucker-Ehrenbrink 2014	HPA-S	MC-ICP-MS	2
[92]	Chacon-Patino et al. 2021	MD	ICP-OES	6
[79]	Duyck et al. 2023	MD	ICP-MS	1
[34]	Ventura et al. 2015	MD	ICP-MS	7
[93]	Kendall et al. 2023	MD + ashing	QQQ–ICP–MS	3
[94]	Wang 2018	MD + ashing	QQQ–ICP–MS	3
[29]	Yang et al. 2017	SRC-MD	ICP-OES & QQQ-ICP-MS	57
[95]	Yang 2019	SRC-MD, Parr bomb acid digestion	ICP-OES & QQQ-ICP-MS	56
[96]	Gao et al. 2017	SRC-MD, Parr bomb acid digestion	ICP-OES & QQQ-ICP-MS	3

Abbreviations: Ref. #—reference number; n (A)—number of elements; ED-XRF—energy-dispersive X-ray fluorescence; DRC—Dynamic Reaction Cell; ICP-MS—inductively coupled-plasma mass spectrometry; GF—graphite furnace; F-AAS—flame atomic absorption spectrometry; HS-GC-MS—headspace gas chromatography mass spectrometry; hTISIS—high-temperature torch-integrated sample introduction system; MFN—Micro-Flow Nebulizer; AES/OES—optical or atomic emission spectrometry; MP—microwave-induced plasma; SF—sector field; MD—microwave digestion; CID—Charge Injection Device; HPA-S—High-Pressure Asher System; ET—Electrothermal; USN—ultrasonic nebulization; HR-CS—high-resolution continuum source; HPD—hotplate acid digestion; HG—hydride generation; AFS—atomic fluorescence spectroscopy; CV—cold vapor; LA—laser ablation; QQQ—triple quadrupole; MIC—microwave-induced combustion; AV—axially viewed; FI—flow injection; IC—ion chromatography system; sp—single particle; N-TIMS—Negative Thermal-Ionization mass spectrometry; MC—Multicollector; PDC—pressurized digestion cavity; SRC—single reaction chamber.

Prior to sampling, the petroleum samples were homogenized in accordance with the certificate recommendations. NIST 1634c (highly viscous) was subjected to gentle heating at 40 °C in a water bath for 1 h, followed by a vigorous shake. To prevent the introduction of water (settled on the bottom), NIST 8505 was stirred at 2/3 of the bottle depth for 10 min at room temperature (24 °C), then left to rest for 10 min; sampling was performed in the middle of the upper half of the homogenized crude oil.

2.2. Digestion Procedures

All sample aliquots were subjected to a series of digestion–evaporation cycles. The digestion was performed in tightly closed vessels under high temperatures (and therefore, elevated pressure) using either a hotplate or a microwave heat source, using a mixture of concentrated nitric acid (conc. HNO_3—65% pure p.a., ChemPur Fine Chemicals and Research Supplies GmbH, Karlsruhe, Germany) and hydrogen peroxide (H_2O_2—30% pure p.a., ChemPur Fine Chemicals and Research Supplies GmbH, Karlsruhe, Germany). Following the final digestion cycle, the resulting solutions were subjected to evaporation in open vessels on a hotplate to near-dryness and then diluted with de-ionized distilled water (diH_2O) with a resistivity of 18.2 MΩ.cm, prepared via a Smart2Pure purification system (Thermo Fisher Scientific, Langenselbold, Germany). All labware vessels used for

the digestion procedures were boiled in conc. HNO_3 for at least 12 h and rinsed with diH_2O prior to use.

2.2.1. Hotplate Digestion (HPD)

A CERAN 500, 22A electric hotplate and 60 mL Savillex perfluoroalkoxy alkane (PFA) screw cap vessels were used for the hotplate digestions. Three aliquots of ca. 0.1 g, 0.2 g and 0.4 g NIST 1634c were placed in the PFA vessels and mixed with 2 mL, 4 mL, and 9 mL conc. HNO_3, respectively. Initially, they were left at room temperature for 24 h, then subjected to a series of hotplate digestion–evaporation cycles (Figure 1). The digestion was performed in tightly closed PFA vessels at ~180 °C (temperature of the hotplate) and evaporation was performed in open PFA vessels at sub-boiling temperatures of <120 °C (temperature of the liquid inside the evaporation vessel) to avoid spills and losses, particularly for elements prone to volatilization when heated, such as Hg, As, Se, Sb, Ni, V, Cr, and Cd [30]). For the 0.1 g, 0.2 g, and 0.4 g aliquots, the total amount of reagents used over the course of ~21 days was 40, 42 and 47 mL, respectively, corresponding to 42 mL, 21 mL, and 12 mL per 0.1 g sample for each of the three aliquot types. The digested solutions were transferred to Falcon polypropylene conical centrifuge tubes and diluted with diH_2O to a volume of 50 mL.

2.2.2. Microwave Digestion (MD)

A 1900-watt Milestone ETHOS EASY microwave with a rotating diffuser, and 100 mL TFM (chemically modified polytetrafluoroethylene, PTFE) containers equipped with a relief valve mechanism were used for the microwave digestion.

Twelve aliquots of NIST 1634c and six aliquots of NIST 8505, ~0.2 g each, were placed in the TFM vessels. Three sets of four NIST 1634c samples and three sets of two NIST 8505 samples were each subjected to 1, 2 or 3 identical microwave digestion cycles (MD-C1, MD-C2, and MD-C3, respectively, Table 2). A single cycle involved adding 9 mL conc. HNO_3 and 1 mL H_2O_2, raising the temperature to 210 °C over the course of 30 min at 1200 W microwave power, maintaining the temperature for 30 min, and cooling over the course of 1 h. Following each cycle, the solutions were transferred to clean PTFE vessels and subjected to slow evaporation at sub-boiling temperatures (temperature of the liquid inside the vessel < 120 °C). After incipient dryness was achieved following the final evaporation, the digested solutions were dissolved in 2 mL conc. HNO_3 then transferred to high-clarity conical centrifuge tubes and diluted with diH_2O to a volume of 50 mL. Additionally, five total analytical blanks (TABs), one for C1, and two each for C2 and C3, were subjected respectively to 1, 2 and 3 cycles of microwave digestion using procedures equivalent to the ones described above.

2.2.3. ICP-MS Analyses

Quantitative analyses were carried out on a Perkin Elmer SCIEX ELAN DRC-e ICP-MS system equipped with a pneumatic cross-flow nebulizer fitted to a cyclonic spray chamber, nickel sampler cone (Perkin Elmer, USA), and nickel skimmer cone (AHF Analysentechnik, Tübingen-Pfrondorf, Germany). The typical ICP-MS operational conditions (Supplementary Table S1) were optimized to provide optimal 24 Mg, 115 In, 238 U intensity and minimal values for CeO^+/Ce^+ and Ba^{2+}/Ba^+ ratios for maximum signal and minimum oxide and double-charged ion formation.

Working calibration solutions were prepared from four Perkin Elmer TruQms ICP-MS multi-element calibration standard solutions with an initial concentration of 10 μg mL^{-1} (Supplementary Table S2). The choice of suitable isotopes for calculating concentrations was based on natural isotopic abundances, potential interferences, calibration coefficients (CC > 0.997), and comparison between the measured isotope values. Based on these criteria,

the following isotopes were selected for calculation of the final published values: ^{24}Mg, ^{27}Al, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{71}Ga, ^{74}Ge, ^{75}As, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{98}Mo, ^{121}Sb, ^{138}Ba, ^{208}Pb, and ^{238}U.

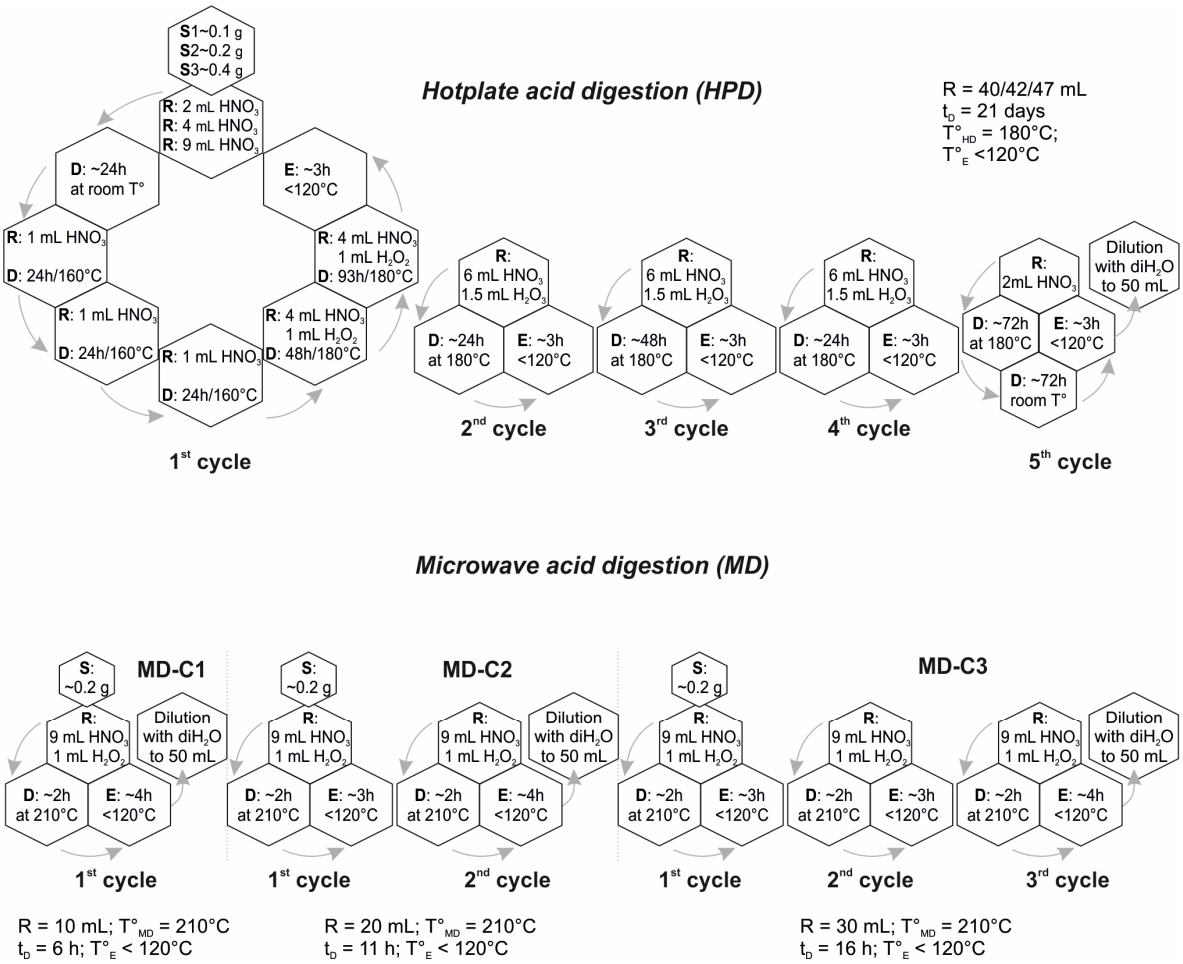


Figure 1. Workflow summary for the hotplate digestion (HPD) and microwave digestion (MD) procedures (S—sample; R—reagents; D—digestion; E—evaporation; t_D—digestion time; $T°_{HD}$—digestion temperature (temperature of the hotplate); $T°_{MD}$—digestion temperature in the microwave; $T°_E$—evaporation temperature (temperature of the liquid inside the evaporation vessel); arrows indicate the sequential cycle steps; dotted lines separate microwave cycles).

Table 2. Sample preparation procedures for 1, 2 and 3 cycles of microwave digestion for NIST 1634c and NIST 8505.

Sample *n*	TAB *n*	Digestion Cycle	MD	Evap.	MD + Evap.	c.HNO_3	H_2O_2	Reagents	Reagents per 0.1 g
1634c/8505			**[h]**	**[h]**	**[h]**	**[mL]**	**[mL]**	**[mL]**	**[mL]**
4/2	1	MD-C1	2	4	6	9	1	10	5
4/2	2	MD-C2	4	7	11	18	2	20	10
4/2	2	MD-C3	6	10	16	27	3	30	15

TAB—total analytical blank; MD—microwave acid digestion; C—cycle; Evap.—evaporation; *n*—number. Note: Digestion parameters for each cycle are as follows: increasing temperature to 210 °C at 1200 W in the course of 30 min; maintaining 210 °C for 30 min; cooling for 60 min.

Limits of detection (LOD) and of quantification (LOQ) were calculated for each element as 3 × SD and 9 × SD, respectively, where SD is the standard deviation (1σ) for five replicate TAB analyses used for correction of the results. In all cases, the LOD and LOQ values were in the ng/g level (Tables 3 and 4).

Table 3. ICP-MS-measured trace element contents (µg mL^{-1}) for NIST 1634c following hotplate and microwave digestion.

	Mg	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Sr	Y	Zr	Mo	Sb	Ba	Pb	U
											SRM & MPV										
SRM & MPV	1.79	2.21	**28.19**	0.19	0.29	34.3	**0.151**	**17.54**	0.35	3.36	n.a.	n.a.	**0.143**	0.42	n.a.	0.004	0.12	0.0080	**1.80**	0.32	0.0039
SD (±)	0.57	1.08	**0.40**	0.09	0.05	10.2	**0.005**	**0.21**	0.23	1.01	n.a.	n.a.	**0.006**	0.11	n.a.	n.a.	0.04	0.01	n.a.	0.14	0.0017
RSD (%)	32	49	**1**	45	17	30	**3**	**1**	66	30	n.a.	n.a.	**4**	26	n.a.	n.a.	31	89.83	n.a.	43	43
n	7	5	-	7	8	12	-	-	10	6	-	-	0	6	-	1	8	2	-	10	4
CS	22	10	-	16	47	40	-	-	15	20	-	-	-	23	-	-	26	2	-	23	9
											HPD										
VIP 008 (~0.1 g)	59.70	26.95	28.26	0.58	1.25	49.06	0.12	17.87	0.47	3.70	0.025	0.009	bdl	1.11	n.a.	0.136	0.16	0.019	1.05	3.98	0.0096
VIP 009 (~0.4 g)	7.93	8.44	28.54	0.60	0.58	46.42	0.12	18.58	0.42	2.45	0.020	0.010	0.09	0.54	n.a.	0.044	0.13	0.013	0.87	1.70	0.0040
VIP 010 (~0.2 g)	20.26	10.55	28.72	0.90	0.66	58.51	0.11	18.13	0.48	3.30	0.022	0.007	0.04	0.72	n.a.	0.068	0.14	0.014	0.94	2.50	0.0036
Mean (*n* = 3)	29.30	15.32	28.51	0.69	0.83	51.33	0.12	18.19	0.46	3.15	0.022	0.009	0.06	0.79	-	0.083	0.15	0.015	0.95	2.73	0.0057
SD (±)	27.04	10.13	0.23	0.18	0.37	6.35	0.007	0.36	0.03	0.64	0.003	0.002	0.03	0.29	-	0.048	0.02	0.003	0.09	1.16	0.0033
RSD (%)	92	66	1	26	44	12	6	2	7	20	13	20	48	37	-	57	12	19	10	42	58
											MD-C1										
VIP 067 (~0.2 g)	0.41	0.43	22.32	0.22	0.21	23.84	0.11	15.37	0.39	2.04	0.018	0.007	0.09	0.25	n.a.	0.004	0.09	0.005	0.96	0.84	0.0032
VIP 068 (~0.2 g)	0.90	0.59	23.03	0.13	0.22	23.59	0.10	15.92	0.35	2.01	0.016	0.008	0.09	0.25	n.a.	0.009	0.08	0.007	0.94	0.22	0.0035
VIP 082 (~0.2 g)	0.33	0.53	23.37	0.20	0.21	26.86	0.12	16.27	0.34	2.07	0.018	0.005	0.09	0.23	n.a.	0.008	0.08	0.007	1.01	0.24	0.0027
VIP 083 (~0.2 g)	0.26	0.62	23.73	0.21	0.23	26.93	0.12	16.56	0.37	2.04	0.022	0.008	0.10	0.27	n.a.	0.006	0.08	0.006	1.02	0.27	0.0032
Mean (*n* = 4)	0.48	0.54	23.11	0.19	0.22	25.30	0.11	16.03	0.36	2.04	0.019	0.007	0.09	0.25	-	0.007	0.08	0.006	0.98	0.39	0.0031
SD (±)	0.29	0.09	0.60	0.04	0.009	1.84	0.007	0.51	0.02	0.02	0.002	0.002	0.004	0.02	-	0.002	0.01	0.001	0.04	0.30	0.0003
RSD (%)	61	16	3	21	4	7	6	3	5	1	13	25	4	7	-	30	7	14	4	76	11
											MD-C2										
VIP 069 (~0.2 g)	0.63	1.04	25.82	0.23	0.26	33.17	0.12	17.90	0.46	2.46	0.021	0.008	0.10	0.26	n.a.	0.010	0.09	0.010	1.13	0.32	0.0033
VIP 070 (~0.2 g)	bdl	1.68	26.95	0.14	0.27	31.86	0.12	18.04	0.48	2.42	0.019	0.010	0.11	0.25	n.a.	0.009	0.10	0.009	1.09	0.33	0.0025
VIP 087 (~0.2 g)	1.18	3.78	32.65	0.31	0.30	48.90	0.14	18.79	0.54	2.54	0.029	0.008	0.13	0.54	n.a.		0.11	0.013	1.98	0.46	0.0032
VIP 088 (~0.2 g)	2.45	3.03	32.56	0.35	0.33	47.76	0.14	18.93	0.54	2.68	0.024	0.009	0.12	0.52	n.a.	0.012	0.09	0.008	1.67	0.45	0.0041
Mean (*n* = 4)	1.42	2.38	29.49	0.26	0.29	40.42	0.13	18.41	0.51	2.52	0.023	0.009	0.12	0.39	-	0.010	0.10	0.010	1.47	0.39	0.0033
SD (±)	0.93	1.25	3.62	0.09	0.03	9.16	0.010	0.52	0.04	0.12	0.004	0.001	0.01	0.16	-	0.002	0.01	0.002	0.43	0.08	0.0007
RSD (%)	66	52	12	37	11	23	8	3	8	5	18	13	12	41	-	16	13	21	29	19	20

Table 3. *Cont.*

	Mg	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Sr	Y	Zr	Mo	Sb	Ba	Pb	U
											MD-C3										
VIP 071 (~0.2 g)	1.21	2.27	31.01	0.36	0.31	41.86	0.15	19.30	0.50	2.52	0.018	0.016	0.13	0.48	n.a.	0.013	0.10	0.010	1.23	0.43	bdl
VIP 072 (~0.2 g)	2.22	1.36	28.68	0.20	0.30	34.84	0.14	20.12	0.45	2.37	0.020	0.010	0.09	0.37	n.a.	0.011	0.10	0.008	1.13	0.34	0.0018
VIP 089 (~0.2 g)	3.73	2.59	32.54	0.09	0.31	46.29	0.13	19.29	0.37	2.47	0.017	0.011	0.13	0.51	n.a.	bdl	0.07	0.008	1.55	0.45	0.0024
VIP 090 (~0.2 g)	2.71	2.89	33.01	0.31	0.31	45.92	0.15	19.38	0.51	2.45	0.023	0.011	0.14	0.58	n.a.	bdl	0.09	0.009	1.73	0.43	0.0014
Mean (n = 4)	2.47	2.28	31.31	0.24	0.31	42.23	0.14	19.52	0.46	2.45	0.019	0.012	0.12	0.48	-	0.012	0.09	0.009	1.41	0.42	0.0019
SD (±)	1.05	0.66	1.95	0.12	0.007	5.32	0.007	0.40	0.06	0.06	0.003	0.003	0.02	0.09	-	0.001	0.02	0.001	0.28	0.05	0.0005
RSD (%)	42	29	6	49	2	13	5	2	14	3	14	23	16	18	-	9	17	14	20	12	27
											MD-ALL										
Mean (n = 12)	1.46	1.73	27.97	0.23	0.27	35.98	0.13	17.99	0.44	2.34	0.020	0.009	0.11	0.38	-	0.009	0.090	0.008	1.29	0.40	0.0028
SD (±)	1.15	1.15	4.27	0.09	0.04	9.71	0.02	1.58	0.07	0.23	0.004	0.003	0.02	0.14	-	0.003	0.012	0.002	0.35	0.16	0.0008
RSD (%)	79	66	15	38	16	27	12	9	17	10	18	29	17	37	-	31	14	26	27	41	28
											HPD & MD										
Mean (n = 16)	7.42	4.45	28.08	0.32	0.38	39.05	0.13	18.03	0.45	2.50	0.021	0.009	0.10	0.46	-	0.028	0.101	0.010	1.22	0.86	0.0035
SD (±)	15.94	6.88	3.79	0.22	0.27	10.97	0.01	1.41	0.07	0.46	0.004	0.002	0.03	0.24	-	0.039	0.026	0.004	0.34	1.07	0.0019
RSD (%)	215	155	13	67	71	28	12	8	15	19	17	27	25	52	-	142	26	37	28	124	56
LOD	0.07	0.04	0.0002	0.005	0.0006	0.02	0.00007	0.002	0.001	0.002	0.00002	0.00002	0.00005	0.002	0.00010	0.0006	0.0006	0.00002	0.0008	0.00018	0.00003
LOQ	0.21	0.11	0.0005	0.014	0.0019	0.06	0.00020	0.007	0.004	0.007	0.00006	0.00006	0.00015	0.006	0.00029	0.0018	0.0018	0.00005	0.0025	0.00054	0.00008

Notes: All values are TAB-corrected. Certificate values—in Bold; SRM—standard reference material; MPV—mean published value; n—number of analyses; CS—confidence score (CS = n/RSD*100); VIP###—sample identifier; HPD—hotplate acid digestion; MD-C1, MD-C2, MD-C3—1-, 2-, and 3-cycle microwave acid digestion; LOD—limits of detection; LOQ—limits of quantification; bdl—below detection limit; n.a.—not available.

Table 4. ICP-MS-measured trace element contents (μg mL^{-1}) for NIST 8505 following microwave digestion.

	Mg	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Sr	Y	Zr	Mo	Sb	Ba	Pb	U
											RM & MPV										
RM & MPV	5.03	1.66	**390**	0.22	0.75	5.11	0.67	50.31	0.20	0.57	0.0348	0.0038	0.209	0.291	0.037	0.07	0.27	0.012	0.42	0.021	0.00060
SD (±)	0.73	1.31	**10**	0.21	0.13	0.93	0.08	2.43	0.17	0.18	0.0018	0.0022	0.006	0.021	0.005	0.05	0.06	n.a.	0.04	n.a.	0.00028
RSD (%)	14	79	**3**	95	18	18	11	5	86	32	5	58	3	7	13	65	22	n.a.	10	n.a.	47
n	5	3	-	6	5	11	3	19	6	3	2	2	3	3	2	5	10	1	6	1	2
CS	35	4	-	6	29	61	27	394	7	9	39	3	105	41	15	8	45	-	61	-	4
											MD-C1										
VIP 073 (~0.2 g)	4.72	bdl	351	0.13	0.60	3.32	0.52	45.10	0.14	0.40	0.029	0.008	0.115	0.152	0.020	0.011	0.26	0.012	0.51	0.009	bdl
VIP 074 (~0.2 g)	3.62	bdl	358	0.13	0.55	2.02	0.54	42.70	0.19	0.52	0.023	0.002	0.139	0.173	0.021	0.009	0.25	0.009	0.39	0.012	bdl
Mean (n = 2)	4.17	-	355	0.13	0.58	2.67	0.53	43.90	0.17	0.46	0.026	0.005	0.127	0.163	0.021	0.010	0.25	0.011	0.45	0.011	-
SD (±)	0.78	-	4.9	0.00	0.03	0.92	0.014	1.70	0.04	0.09	0.004	0.004	0.017	0.015	0.0003	0.0013	0.011	0.0021	0.08	0.0024	-
RSD (%)	19	-	1	2	6	34	3	4	22	19	15	86	13	9	1	13	4	19	18	22	-

Table 4. *Cont.*

	Mg	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Sr	Y	Zr	Mo	Sb	Ba	Pb	U
											MD-C2										
VIP 075 (~0.2 g)	2.50	bdl	384	0.12	0.70	3.87	0.59	48.98	0.24	0.64	0.030	0.004	0.115	0.168	0.025	0.011	0.30	0.013	0.51	0.019	bdl
VIP 076 (~0.2 g)	2.39	bdl	361	0.17	0.60	1.18	0.57	45.32	0.21	0.39	0.033	0.008	0.135	0.167	0.023	0.008	0.27	0.010	0.49	0.022	bdl
Mean (n = 2)	2.44	-	373	0.15	0.65	2.53	0.58	47.15	0.22	0.51	0.032	0.006	0.125	0.168	0.024	0.009	0.28	0.011	0.50	0.021	-
SD (±)	0.07	-	16.8	0.03	0.07	1.90	0.016	2.59	0.02	0.17	0.002	0.003	0.014	0.001	0.0010	0.0025	0.015	0.0021	0.02	0.0020	-
RSD (%)	3	-	5	22	11	75	3	5	8	34	8	45	11	0	4	27	5	18	4	10	-
											MD-C3										
VIP 077 (~0.2 g)	2.16	bdl	429	0.08	0.70	6.00	0.65	50.80	0.27	0.39	0.033	0.006	0.156	0.341	0.016	0.017	0.32	0.017	0.57	0.044	bdl
VIP 078 (~0.2 g)	2.09	bdl	412	0.05	0.67	4.88	0.63	50.79	0.19	0.30	0.033	0.010	0.144	0.243	0.017	0.016	0.27	0.008	0.60	0.134	bdl
Mean (n = 2)	2.12	-	421	0.06	0.69	5.44	0.64	50.79	0.23	0.34	0.033	0.008	0.150	0.292	0.016	0.016	0.30	0.013	0.59	0.089	-
SD (±)	0.04	-	11.5	0.02	0.03	0.80	0.011	0.01	0.05	0.06	0.0005	0.003	0.008	0.069	0.0001	0.0007	0.03	0.007	0.02	0.064	-
RSD (%)	2	-	3	30	4	15	2	0	24	19	1	34	5	24	1	5	12	52	3	72	-
											MD-ALL										
Mean (n = 6)	2.91	-	383	0.11	0.64	3.55	0.58	47.28	0.21	0.44	0.030	0.006	0.134	0.208	0.020	0.012	0.28	0.012	0.51	0.040	-
SD (±)	1.05	-	31.8	0.04	0.06	1.78	0.05	3.38	0.04	0.12	0.004	0.003	0.016	0.073	0.004	0.004	0.03	0.003	0.07	0.047	-
RSD (%)	36	-	8	38	10	50	9	7	21	28	13	46	12	35	17	30	9	29	14	118	-
LOD	0.07	0.04	0.0002	0.005	0.0006	0.02	0.0001	0.002	0.001	0.002	0.00002	0.00002	0.00005	0.002	0.0001	0.0006	0.0006	0.00002	0.0008	0.0002	0.00003
LOQ	0.21	0.11	0.0005	0.014	0.0019	0.06	0.0002	0.007	0.004	0.007	0.00006	0.00006	0.00015	0.006	0.0003	0.0018	0.0018	0.00005	0.0025	0.0005	0.00008

Notes: All values are TAB-corrected. Symbols are as in Table 3. RM—research material.

3. Results and Discussion

3.1. Characteristics of the Digested Solutions

The digested solutions were inspected for clarity, color, residue, and the tendency to foam upon agitation following final dilution.

3.1.1. Characteristics of Hotplate-Digested NIST 1634c Solutions

Following the initial hotplate digestion cycle, reddish-brown gas was released upon the opening of the vessels, and the solutions were dark brown with readily visible dark specks of undigested residue. With each successive digestion cycle, the solutions became lighter and clearer, eventually turning light yellow and transparent. The color intensity and the residue amount were evidently controlled by the initial sample amount as a function of the total amount of reagents used—larger samples received relatively lower amounts of reagents and had darker color and more residue compared with smaller samples. Following the final dilution of the digested HPD samples with diH_2O, all solutions were transparent, with a slight yellow hue that remained more pronounced for the larger samples. It is worth noting that a single sample subjected to a modified, shorter hotplate digestion procedure (HPD-S) was slightly cloudy, and following agitation, developed stable foam on top that could be observed for more than 1 h (Figure 2A,B; Supplementary Table S3).

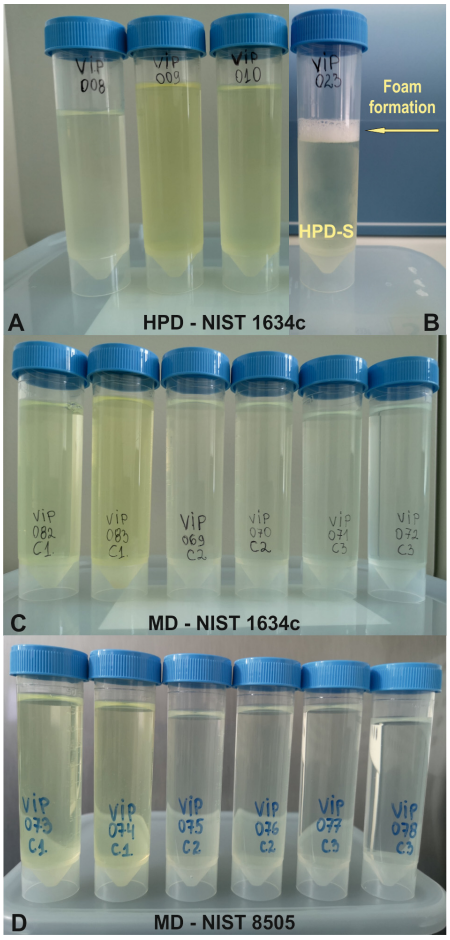


Figure 2. Characteristics of acid-digested and diH_2O-diluted samples. Panels (**A**,**B**) show hotplate-digested NIST 1634c with foam formation (**B**) in HPD-S (Supplementary Table S3); Panels (**C**,**D**) show microwave-digested NIST 1634c and NIST 8505 samples following 1, 2 and 3 digestion cycles (C1, C2, and C3, respectively).

3.1.2. Characteristics of Microwave-Digested NIST 1634c and NIST 8505 Solutions

Intense reddish-brown gas was released upon opening of the vessels following one cycle of microwave digestion (MD-C1) for both the NIST 1634c and NIST 8505 samples. The solutions were golden-yellow to dark-yellow and slightly cloudy. Dark, undigested specks were observed at the bottom of one of the NIST 1634c vessels, but none for NIST 8505. The final diluted solutions were light-yellow to medium-yellow in color (Figure 2C,D). Bubbles that formed on the surface of the diluted samples following agitation dissipated in 1–3 min. Upon opening of the vessels following the second cycle (MD-C2), a small amount of dark-orange gas was released from the NIST 1634c samples; no visible gases were observed for NIST 8505; nevertheless, pressure could be felt upon opening. After the third microwave cycle (MD-C3), no gases were released, and no pressure was felt upon opening of the containers. Two- and three-cycle solutions were indistinguishable to the naked eye, having a bright lemon-yellow to light lemon-yellow color and clear appearance. The final diluted solutions were pale yellow (NIST 1634c) to nearly colorless (NIST 8505). Stable foam would not form following agitation (Figure 2C,D).

3.2. Trace Element Contents

ICP-MS-measured trace element abundances for NIST 1634c and NIST 8505 from this study are listed in Tables 3 and 4, respectively. Also provided are certificate values as well as mean published values (MPVs) for elements not covered in the certificate (discussed in detail in Section 4).

All trace element data were TAB-corrected. Following microwave digestion, most trace metals in all five total analytical blanks (TABs) were within 3 ng mL^{-1}, except for the Mg, Al, and Fe blanks, which were higher (Mg: 30–60–86 ng mL^{-1}, Al: 16–29–45 ng mL^{-1}, Fe: 17–26–32 ng mL^{-1}) (Figure 3). Notably, trace element abundances in the TABs consistently increase with each successive MD cycle (Figure 3). For example, TE concentrations are ~2× higher in the C2 TABs and ~3× higher in the C3 TABs compared with the C1 TAB. This correlation across all measured elements identifies the reagents used for digestion as the main source of analytical blank. The consistency in TAB measurements also shows negligible contribution from other sources (e.g., water used for cleaning, rinsing and dilution; random lab contamination, etc.) and strengthens the validity of TAB corrections. Although total analytical blanks were not performed for hotplate digestions, HPD measurements were also TAB-corrected based on the amount of reagents used for their digestion and their respective metal contents as analyzed in the MD blanks (Table 3).

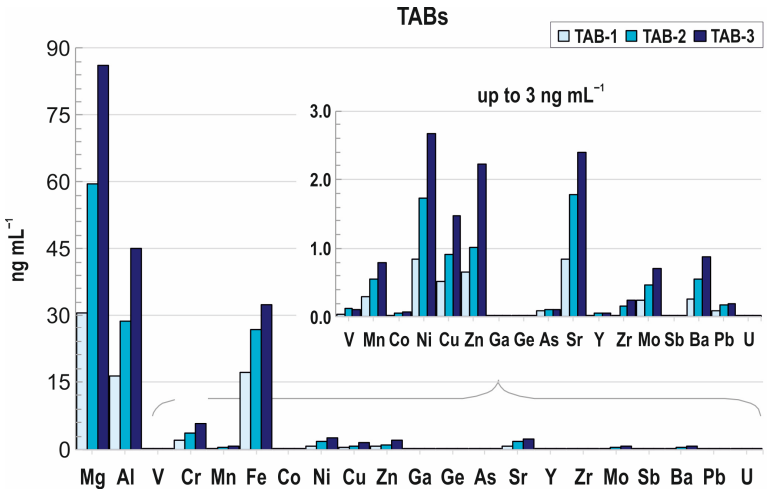


Figure 3. Trace element composition of total analytical blanks for 1 cycle (TAB-1, n = 1), 2 cycles (TAB-2, n = 2) and 3 cycles (TAB-3, n = 2) of microwave digestion; n—number of analyses.

3.2.1. Trace Element Contents for NIST 1634c

Trace element contents for NIST 1634c range from ca. 60 μg mL^{-1} to less than 0.01 μg mL^{-1} (Table 3). Magnesium (60 μg mL^{-1}), Fe (59 μg mL^{-1}), V (33 μg mL^{-1}), Al (27 μg mL^{-1}), and Ni (20 μg mL^{-1}) are among the most abundant (Figure 4A), whereas most of the remaining elements are within 1 μg mL^{-1}, with Ga, Ge, Zr, Sb, and U being the least abundant (<0.1 μg mL^{-1}).

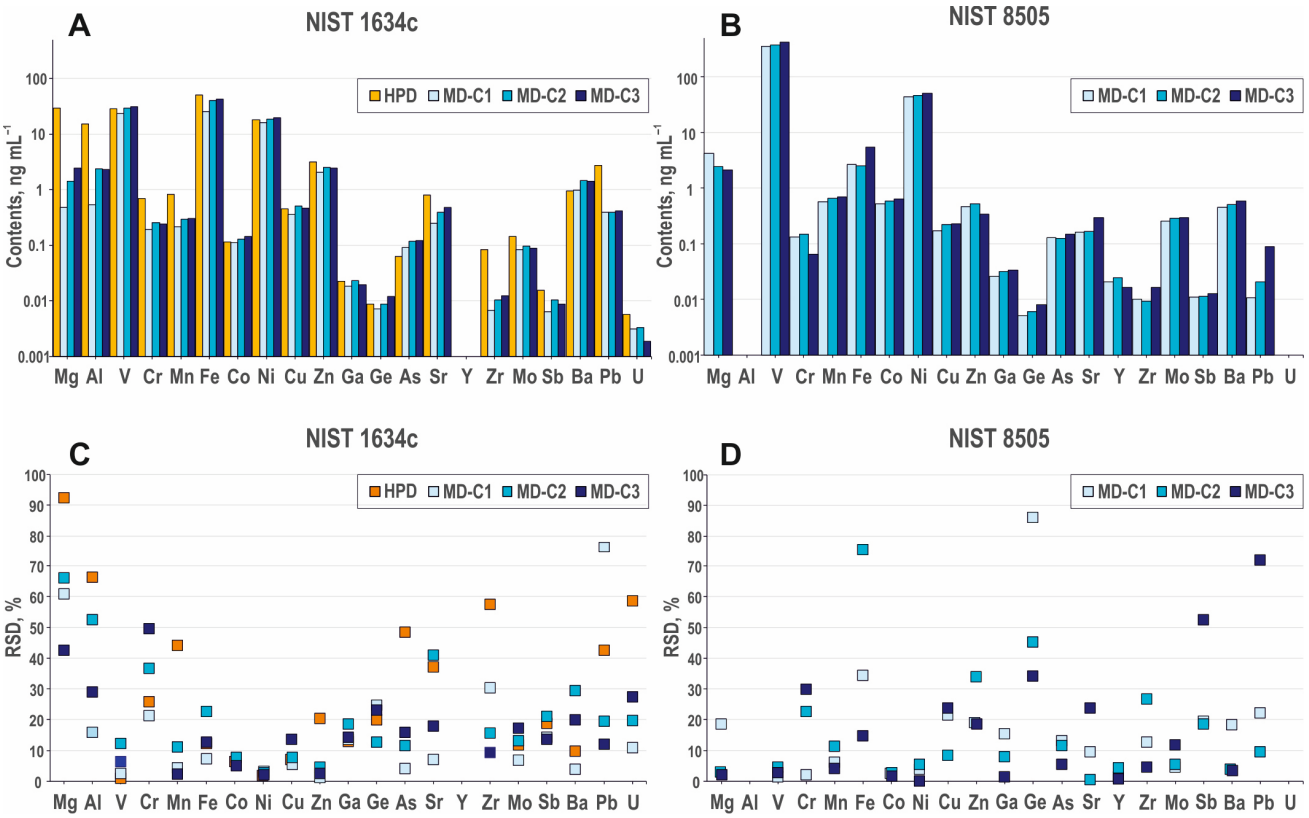


Figure 4. ICP-MS-measured trace element concentrations for NIST 1634c (**A**) and NIST 8505 (**B**), following different digestion procedures. Panels (**C**,**D**) show the variance (RSD%) for each element.

HP digestion yielded overall similar concentrations to the two- and three-cycle MDs and consistently higher concentrations compared with one-cycle MDs. Prominent exceptions are Mg and Al, with 8 to 60 μg mL^{-1} in HPD, compared with 0.3–3.8 μg mL^{-1} in all MD samples. On the other hand, certain elements like V, Ni, Co, As, and Ba ± Cu, Ge, and Ga, have either similar or slightly higher values in MD (C2 and C3) compared with HPD. Within the MD series alone, C2 and C3 yielded consistently higher abundances compared with C1, mostly observed for Mg, Al, and Fe, followed by V, Ni, Ba, Zn, Mn, Cr, Cu, and Sr.

The variance for most elements (V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Mo, Sb, and Ba) across both HPD and MD measurements is predominantly within 20% RSD (except for hotplate digestion for Mn (44% RSD) and As (48% RSD). Nickel, Co, and V have consistently low scatter in all digestion groups, typically below 8% RSD (Figure 4D), whereas scatter for Mg and Al is invariably high, with RSDs mostly above 40% (and up to 92% within the hotplate digestion). The scatter for Sr, Zr, Pb, and U is variable, with RSDs either lower or higher than 20%. Notably, microwave digestion resulted in more consistent measurements (three to five elements with RSDs > 25%) compared with hotplate digestion (nine elements with RSDs > 25%). Furthermore, variance within HPDs is significant for certain elements like Mg (92%), Al (66%), U (58%), Zr (57%), and Mn (44%), and is usually considerably

higher compared with MD. Within the MD series alone, scatter increases in the order C1 < C3 < C2 (Table 3).

3.2.2. Trace Element Contents for NIST 8505

Measured trace element contents for NIST 8505 range from ~430 µg mL−1 to <0.01 µg mL^{-1} (Table 4). Most abundant are V (429 µg mL^{-1}) and Ni (51 µg mL^{-1}), followed by Fe (6 µg mL^{-1}) and Mg (4.7 µg mL^{-1}), whereas most other elements are below 1 µg mL^{-1}, with Ga, Ge, Y, Zr, and Sb being the least abundant (<0.05 µg mL^{-1}). A distinct pattern of progressively increasing values with each successive microwave cycle is established for most elements (Figure 4C). Magnesium is an exception, following a reverse pattern, whereas Fe, Cr, Zn, Y, and Zr exhibit mixed patterns (Table 4). The variance for V, Co, Ni, and Y is low (<5% RSD), and for most elements within each of the MD cycles, RSD is <20% (often <15%). Prominent exceptions are Ge, Fe, and Pb, with up to 86%, 75%, and 72% RSD, respectively (Figure 4D).

3.3. Elemental Recoveries

To examine the efficiency of the petroleum digestion procedures used in this study, we compared the ICP-MS measurements for both studied materials with the corresponding certificate values. The NIST 1634c certificate provides certified values for V (28.19 ± 0.40 µg mL^{-1}), Ni (17.54 ± 0.21 µg mL^{-1}) and Co (0.1510 ± 0.0051 µg mL^{-1}); a reference value for As (0.1426 ± 0.064 µg mL^{-1}); and an information value for Ba (1.8 µg mL^{-1}). The NIST 8505 certificate provides a recommended value for V alone (390 ± 10 µg mL^{-1}). The contents of the remaining 15 elements for NIST 1634c and 19 elements for NIST 8505 analyzed in this study were compared with mean values from published data (MPV; Table 5). To calculate the MPVs, we used our newly presented compilation of published values for trace elements, with a 2σ filter applied to the dataset (Tables 3 and 4; unfiltered data provided in the Supplementary Tables S4 and S5). The presented values were obtained by various digestion methods, such as microwave digestion, a High-Pressure Asher system, and direct dilution and emulsion, as well as various analytical techniques, predominantly ICP-MS, followed by ICP-OES/AES and GF-AAS (Table 1). As such, the MPVs, even though not certified values, provide a useful estimate for the trace element contents of the two studied petroleum materials and a reference point for comparison.

3.3.1. Recoveries for NIST SRM 1634c

Comparison with certificate values. For all five elements provided in the certificate, recoveries for C2 and C3 digestions fall approximately within ±20% of the certificate values, with the best matches for V (105/111%) and Ni (105/111%), followed by Co (86/94%), As (83/85%), and Ba (82/78%) (Table 5, Figure 5A). One-cycle digestion also yielded reasonable recoveries for V (82%) and Ni (91%); lower recoveries for Co (73%); and particularly low for As (64%) and Ba (55%). Hotplate-digested samples revealed the closest matches for V (101%) and Ni (104%), lower recoveries for Co (77%), and significantly lower recoveries for As (45%) and Ba (53%). Corresponding to the systematic increase in measured contents from one-cycle through two- and three-cycle microwave digestion, we observe a noticeable progressive increase in recovery rates in the same direction (with the exception of Ba). Furthermore, there is a distinct tendency for both higher and usually better recoveries for V and Ni compared with Co and, particularly, As and Ba across all digestion groups. Notably, this trend is paralleled by the relatively low variance for V, Ni, and Co and higher variance for As and Ba (Table 3).

Table 5. Certificate-based and MPV-based trace element recoveries for NIST 1634c and NIST 8505.

	Mg	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Sr	Y	Zr	Mo	Sb	Ba	Pb	U
NIST 1634c																					
SRM & MPV																					
SRM & MPV	1.8	2.2	**28.2**	0.19	0.29	34.3	**0.151**	**17.5**	0.35	3.36	n.a.	n.a.	**0.143**	0.42	n.a.	0.004	0.12	0.008	**1.8**	0.32	0.0039
SD (±)	0.6	1.1	**0.4**	0.09	0.05	10.2	**0.005**	**0.21**	0.23	1.01	n.a.	n.a.	**0.006**	0.11	n.a.	n.a.	0.04	0.01	n.a.	0.14	0.0017
RSD (%)	32	49	**1**	45	17	30	**3**	**1**	66	30	n.a.	n.a.	**4**	26	n.a.	n.a.	31	90	n.a.	43	43
n	7	5	**-**	7	8	12	**-**	**-**	10	6	-	-	**-**	6	0	1	8	2	**-**	10	4
CS	22	10	**-**	16	47	40	**-**	**-**	15	20	-	-	**-**	23	-	-	26	2	**-**	23	9
HPD																					
Mean (*n* = 3)	1634	692	101	360	285	149	77	104	132	94	-	-	45	190	-	2022	123	194	53	858	149
SD (±)	1508	458	1	93	126	19	5	2	9	19	-	-	22	71	-	1162	14	37	5	364	87
MD-C1																					
Mean (*n* = 4)	27	24	82	100	75	74	73	91	105	61	-	-	64	60	-	164	70	80	55	123	81
SD (±)	16	4	2	21	3	5	5	3	6	0.7	-	-	3	4	-	50	5	11	2	94	9
MD-C2																					
Mean (*n* = 4)	79	108	105	135	100	118	86	105	146	75	-	-	83	95	-	250	82	130	82	122	86
SD (±)	52	56	13	49	11	27	7	3	11	3	-	-	10	39	-	39	11	27	24	24	17
MD-C3																					
Mean (*n* = 4)	138	103	111	125	105	123	94	111	133	73	-	-	85	116	-	299	75	109	78	131	48
SD (±)	58	30	7	62	2	15	5	2	18	2	-	-	14	21	-	28	13	15	16	16	13
NIST 8505																					
RM & MPV																					
RM & MPV	5.0	1.7	**390**	0.22	0.75	5.11	0.67	50.3	0.20	0.57	0.035	0.004	0.209	0.29	0.037	0.07	0.27	0.012	0.42	0.021	0.0006
SD (±)	0.7	1.3	**10**	0.21	0.13	0.93	0.08	2.43	0.17	0.18	0.002	0.002	0.006	0.02	0.005	0.05	0.06	n.a.	0.04	n.a.	0.0003
RSD (%)	14	79	**3**	95	18	18	11	5	86	32	5	58	3	7	13	65	22	n.a.	10	n.a.	47
n	5	3	**-**	6	5	11	3	19	6	3	2	2	3	3	2	5	10	1	6	1	2
CS	35	4	**-**	6	29	61	27	394	7	9	39	3	105	41	15	8	45	-	61	-	4
MD-C1																					
Mean (*n* = 2)	83	-	91	61	76	52	79	87	86	80	75	134	61	56	56	15	94	94	108	53	-
SD (±)	15	-	1	1	5	18	2	3	19	15	12	115	8	5	1	2	4	18	20	12	-
MD-C2																					
Mean (*n* = 2)	49	-	96	68	86	49	87	94	114	90	91	162	60	58	66	13	104	98	120	101	-
SD (±)	1	-	4	15	10	37	2	5	10	30	7	73	7	0.3	3	4	6	18	5	10	-
MD-C3																					
Mean (*n* = 2)	42	-	108	30	91	106	96	101	116	59	95	211	72	100	45	23	109	110	140	433	-
SD (±)	1	-	3	9	4	16	2	0.02	28	11	1	72	4	24	0.4	1	13	57	5	310	-

Note: Symbols are as in Tables 3 and 4.

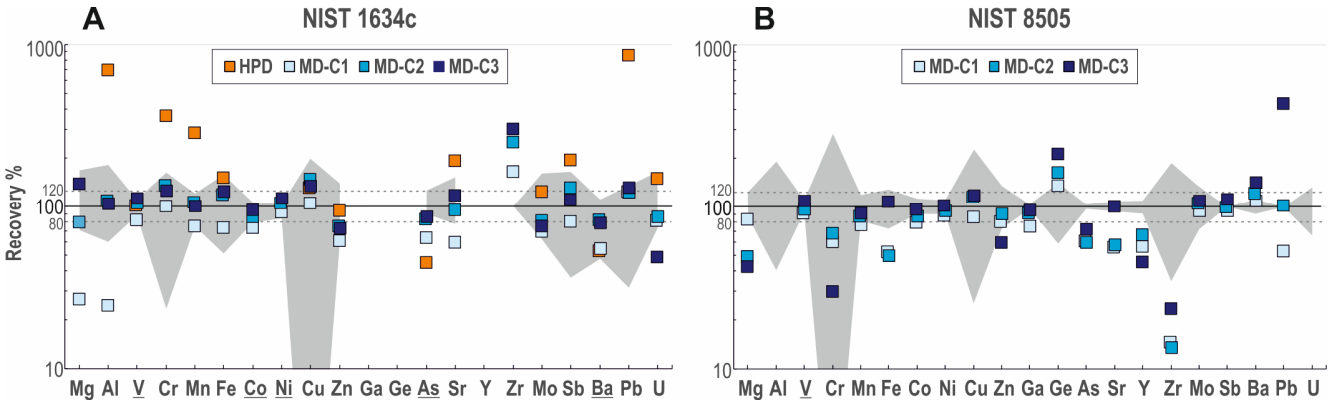


Figure 5. Certificate-based (underlined elements) and MPV-based trace element recoveries for NIST 1634c (**A**) and NIST 8505 (**B**); gray field covers published values.

Comparison with mean published values (MPVs). The majority of published data for NIST 1634c are for trace elements provided in the certificate like Co, As, Ba, and particularly Ni and V (Supplementary Table S4). Published values for V and Ni have low variance (5% RSD), whereas Co, As and particularly Ba exhibit relatively larger scatter (10%, 12%, and 28%RSD, respectively). Although this could be partly attributed to the larger number of measurements for V (n = 59) and Ni (n = 55) compared with Co (n = 21), As (n = 19), and Ba (n = 11), this relationship is not universally valid for all reported elements.

From the remaining analyzed elements not covered in the certificate, the ones most often reported in the literature are Fe, Cu, and Pb (n = 10–12), followed by Mn, Mo, Cr, Mg, Zn, Sr, Al, and U (n = 4–8), Sb (n = 2) and Zr (n = 1); Ga, and Ge are not reported. The variance for these elements ranges from 17% (Mn) to 90% RSD (Sb) but mostly falls within 30–45%. The significant scatter for certain elements can be attributed to multiple factors, among which the different digestion methods and analytical equipment, as well as the small number of measurements.

The larger the number of published values and the lower the variance for a certain element, the higher the confidence in its mean value (MPV). Thus, the number of analyses expressed as a percentage of the RSD may be a useful marker for estimating the potential validity of a given MPV, i.e., a confidence score (CS = n/RSD × 100). The higher the CS value, the better the chances for an MPV being closer to the "true" value. In this respect, confidence scores for MPVs in our dataset for elements not reported in the certificates, in descending order, are as follow: Mn (47), Fe (40), Mo (26); Sr, Pb, Mg, and Zn (23–20); Cr, Cu (16–15); Al, U (10–9), and Sb (2) (Table 3).

For most elements, MPV-based recoveries for C2 and C3 microwave digestion are within ±30% of the mean published value, and mostly within ±20%, except for Cr (125–135%), Mg (79–138%), Cu (133–146%), and particularly Zr (250–300%) (Table 5). Note that Cr, Mg and Cu have a relatively low confidence score, whereas Zr has a single reported value. One-cycle microwave digestion, in general, yielded low MPV-based recoveries, mostly within ±40% (60–123%) of the mean published value, and particularly low recoveries for Al (24%) and Mg (27%). Nevertheless, many elements like Mn, Fe, Pb, U, Cr, Cu, and Sb in the one-cycle microwave digestion are still within a ±25% match (74–123%). In contrast HPD samples yielded consistently and significantly higher MPV-based recoveries—usually well above 150%, and up to ~1600% for Mg, and ~2000% for Zr (Figure 5A).

Additionally, the number of elements falling within ±20% of the mean published values is highest for C2 (11 elements) and C3 (8 elements), followed by C1 (6 elements) and, lastly, by HP digestion (3 elements). A similar pattern is revealed for recoveries within

±10% of the mean published values (5, 4, 3, and 3, respectively), as well as ±25% (14, 12, 8, and 4, respectively). Overall, these trends in MPV-based recoveries suggest that microwave digestion, and particularly the two- and three-cycle versions, yield better results than the hotplate digestion.

A weak but systematic inverse correlation between sample weight and recovery values is observed within the HPD samples—smaller samples have slightly better recoveries for most certificate elements (except for As) compared with larger samples (Supplementary Table S6).

3.3.2. Recoveries for NIST RM 8505

For all three groups of MW digestions, the recoveries for V (the sole element provided in the certificate) are within ±9% of the recommended value, with the closest match for C2 (96%), followed by C3 (108%) and C1 digestions (91%). Again, we observe the lowest recoveries in C1 and progressively higher ones in C2 and C3 samples (Table 5, Figure 5B).

Published trace element values for NIST 8505 are dominated by V (n = 31) and Ni (n = 19), followed by Fe, Mo, Ba, Cr, Cu, Mn, Mg, and Zr (n = 5–11). Arsenic, Sr, Co, Zn, Al, Ge, Ga, and Y (n = 2–3) are scarcely reported, whereas Sb and Pb each have a single reported value (Supplementary Table S5).

In descending order, confidence scores (CS) for NIST 8505 MPVs in our dataset are as follows: Ni (394), As (105), Ba, Fe (61), Mo, Sr (45–41), Ga, Mg (39–35), Mn, Co (29–27), Y (15), Zn, Zr, Cu, Cr (9–6), and Ge (3).

Many elements have a ± 25% overlap with MPVs, with the best matches for Mo (±9%), Sb (±10%), Ni (±13%), Cu (±16%), and Co (±21%), followed by Mn (±24%), Ga (±25%), ± Ba, and Zn (±20% for all digestions except C3). A distinct pattern of progressively increasing values from C1 through C2 and C3 is established for the above elements. Except for Ge, which shows elevated MPV-based recoveries (>130%), the remaining elements (As, Fe, Sr, Mg, Y, Zr, Cr, Pb) usually have lower values than the mean published values (usually <66%); furthermore, the aforementioned pattern is usually not observed for these elements (Table 5; Figure 5B). All three digestion groups have the same number of elements (11) with MPV-based recoveries within ±25%. However, with each successive cycle, there is an increasing number of elements with recoveries in the range ±10% (four, seven, and nine elements for C1, C2, and C3 respectively) (Table 5).

3.4. Digestion Efficiency

Our assessment of the degree of digestion primarily considers certificate-based recoveries. Additionally, we compare our measurements with the mean published values (MPV) for trace elements not covered in the certificates, and also consider the variance of our measurements (RSD), as well as observable characteristics of the digested solutions.

3.4.1. Digestion Efficiency for NIST 1634c

According to the level of agreement between our measurements with the certificate values for V, Ni, Co, As, and Ba and with the mean published values for elements not covered in the certificate, the two- and three-cycle versions of microwave acid digestion stand out with the best outcomes, arguably achieving the highest level of decomposition (Table 5, Figure 5A). These two digestion procedures are characterized by recoveries between 82 and 105% (MD-C2) and 78–111% (MD-C3) for the elements from the certificate, and between 75 and 130% (MD-C2) and 73–133% (MD-C3) for most of the remaining elements. Conversely, the recoveries for one-cycle microwave digestion are overall lower—within 55–91% for elements from the certificate and 24–123% for most of the remaining elements suggest insufficient sample digestion. Hotplate digestion yielded mixed results for certificate elements (45–104%), including the best matches for V and Ni, but had relatively lower

recoveries for Co, As, and Ba (Figure 5A). At the same time, MPV-based recoveries for most of the remaining elements are considerably higher for the HPD procedure (94–2022%; Figure 5A, Table 5). This complex pattern suggests possible underdigestion, combined with some degree of contamination and/or losses during the digestion procedure. The number of elements falling within a certain percentage of the certificate- and MPV-based values taken as a baseline for comparison further reinforces the above observations. For example, 11 elements from C2, 8 elements from C3, 6 elements from C1, and 3 elements from HPD procedures fall within ±20% of the expected values.

In addition, the microwave digestion, in general, stands out with less scatter (Table 3; Figure 4C). For example, two- and three-cycle microwave digestions have four to five elements with RSDs > 25%, compared with nine elements for the hotplate digestion. Furthermore, HPD has significant variance (>40% RSD) for seven elements (Mg, Al, U and Zr), whereas each microwave digestion has two elements (Mg ± Al, Pb, or Cr) with variance > 40% RSD (Table 3). These show that the two- and three-cycle MD versions result in more reproducible concentrations than the HPD.

The characteristics of the digested liquids, like transparency, color, and foaming, further support the above—solutions that were free from residue and foam, and were of the highest clarity and the lightest color, such as the two- and three-cycle MDs (Figure 2D) resulted in the best recoveries. Notably, HPD-S (a single sample subjected to a modified, shorter hotplate digestion procedure, which was slightly cloudy and formed stable foam upon agitation) had the largest deviation from certificate values (52–145%, Supplementary Table S6).

Another takeaway from the HPD alone is that the color intensity of the digested solution and the residue amount were clearly controlled by the initial sample amount as a function of the total amount of reagents used—smaller samples received relatively larger amounts of reagents and had lighter color compared with larger samples, arguably resulting in better digestion. The latter is supported by the slightly better recoveries in smaller samples for V, Ni, Co, and Ba (Supplementary Table S6).

3.4.2. Digestion Efficiency for NIST 8505

The recoveries for V, the sole recommended value in the NIST 8505 certificate, are within ±9%, with a steady increase from C1 (91%), through C2 (96%), and C3 (108%). Comparison with MPVs reveals a similar pattern of gradual rise in recovery values for most elements with each consecutive microwave cycle, suggesting progressive levels of digestion in the same direction. All three digestion groups have the same number of elements (11) with recoveries within ±25% of the expected value. However, with each successive cycle, there is an increasing number of elements falling within ±10% (four, seven, and nine elements for C1, C2, and C3 respectively; Table 5).

Within all three groups of MD, the variance for most elements is within 20% RSD, with the least scatter for V, Ni, Co, and Y (within 5% RSD), followed by Mo, Mn, Ga, As, Ba, and Mg (1–19% RSD), and more significant scatter for Ge, Fe, Sb, Pb, and Zn (10–86% RSD). Variance is generally larger for C1, with C2 and C3 digestions having a greater number of elements within 10% RSD (10 and 9 elements respectively) compared with C1 samples (8 elements, Table 4). Additionally, C2 and C3 solutions were clearer and lighter in color compared with C1 digestions, further supporting a higher degree of decomposition (Figure 2D). Based on all the above, the two- and three-cycle MDs were more efficient compared with the one-cycle MD.

3.5. Updated Trace Element Composition for NIST 1634c and NIST 8505

The two studied oils, NIST 1634c and NIST 8505, are the two most widely used reference materials for trace metal contents in petroleum [7,9,25,36–38,67] (Table 1). However, these two materials are characterized by NIST only for a limited number of trace metals—nine for NIST 1634c and one for NIST 8505. As a result, despite their wide use, their trace metal contents for most elements remain insufficiently characterized. At the same time, their trace metal content has been reported in a number of publications (Table 1), but these data have never been systematically summarized and compared. Here, we aim to better characterize the elemental composition of the two reference materials by integrating new data from MD-C2 and MD-C3 digestion with our newly presented compilation of published data for NIST 1634c and NIST 8505 (Tables 3 and 4; Supplementary Tables S4 and S5). The mean value for each element from this combined dataset represents a useful approximation for the "true" content of the elements and can be used as a non-certified reference point for trace metal research on petroleum. To eliminate potential outliers from the large dataset that includes various methods and equipment, we applied a 2σ filter (Table 6); unfiltered data are also available (Table 6; Supplementary Tables S4 and S5). In addition, data considered unacceptable by the authors, as well as data reported above or below a certain limit (e.g., S > 2000 μg mL^{-1} in [34] 2015; Ti < 0.01 μg mL^{-1}, Ag < 0.02 μg mL^{-1}, Sn < 0.21 μg mL^{-1} in [46]), were excluded from the mean value calculations.

3.5.1. Updated Trace Element Composition for NIST 1634c

In our NIST 1634c compilation, we included data for 37 elements from 59 publications, augmented with 18 overlapping elements from this study, as well as our data for 2 more elements (Ga and Ge) reported only in this study, bringing the total to 39 elements (Table 6). After 2σ filtering, V (n = 58) and Ni (n = 52) followed by Co (n = 23) and As (n = 21) have the largest number of reported values, followed by Na, Mg, Al, S, Cl, Ca, Cr, Mn, Fe, Cu, Zn, Se, Sr, Mo, Cd, Sb, Ba, Pb, U (n = 4–14), whereas the remaining 16 elements have only few reported measurements ($n \leq 3$). Approximately half of the elements in the updated NIST 1634c compilation demonstrate relatively low scatter (RSD ≤ 25%, Table 6). Among them, the most widely used and certified elements (V, Ni, Co) show the lowest variance (RSD < 10%, usually within 5%). The rest of the elements usually have RSDs between 28% and 58% and rarely above 72%.

A comparison between the mean values from the updated compilation and certificate values reveals the best matches are for V, Ni, Cl, and As (100%, 99%, 102%, and 103% respectively), followed by Se (105%), S (105%), Na (95%), Co (94%), and Ba (82%), a pattern similar to the one produced by the results in this study (except for As). Overall, this favorable match between mean published values and certificate values for NIST 1634c suggests that the remaining compiled mean values represent a good approximation for the composition of this reference material.

3.5.2. Updated Trace Element Composition for NIST RM 8505

In the NIST 8505 compilation, we included data for a total of 63 elements from 24 publications, with the addition of 19 overlapping elements from this study (Table 6). After 2σ filtering, the largest number of analyses are for V (n = 33), Ni (n = 19), Mo (n = 12), and Fe (n = 12), followed by B, Mg, S, K, Ca, Cr, Mn, Co, Cu, Zn, Ga, Ge, As, Sr, Y, Zr, Ba, Re, Os (n = 4–8), together comprising approximately 1/3 of the elements in the updated compilation (Table 6). The remaining 40 elements (~2/3 of the compilation) have fewer measurements ($n \leq 3$), and for 10 of them (N, Si, Ru, Pd, Sn, Cs, Hf, Ta, Ir, Pt) there is a single reported value [29,90].

Table 6. Updated elemental composition for NIST SRM 1634c and NIST RM 8505.

	NIST 1634c										NIST 8505									
	n	***n***	**Mean**	**Mean**	**SD (±)**	**SD (±)**	**RSD**	**RSD**	***n*/RSD**	***n*/RSD**	***n***	***n***	**Mean**	**Mean**	**SD (±)**	**SD (±)**	**RSD**	**RSD**	***n*/RSD**	***n*/RSD**
	No Filter	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**
			ppm	**ppm**	**ppm**	**ppm**	**%**	**%**	**%**	**%**			**ppm**	**ppm**	**ppm**	**ppm**	**%**	**%**	**%**	**%**
H	-	-	-	-	-	-	-	-	-	-	2	2	106,800	106,800	1,697	1,697	2	2	126	126
Li	-	-	-	-	-	-	-	-	-	-	2	2	0.010	0.010	0.010	0.010	107	107	2	2
Be	2	2	0.025	0.025	0.013	0.013	53	53	4	4	2	2	0.0028	0.0028	0.0004	0.0004	13	13	16	16
B	-	-	-	-	-	-	-	-	-	-	4	4	0.6	0.6	0.6	0.6	94	94	4	4
C	-	-	-	-	-	-	-	-	-	-	2	2	854,450	854,450	636	636	0.07	0.07	2,685	2,685
N	-	-	-	-	-	-	-	-	-	-	1	1	4,100	4,100	-	-	-	-	-	-
Na		-		**37**		-		-		-	3	3	8.0	8.0	4.6	4.6	57	57	5	5
Mg	10	8	2.7	1.7	2.9	0.4	107	23	9	35	7	7	4.2	4.2	1.5	1.5	35	35	20	20
Al	8	7	3.6	2.2	3.9	0.9	108	39	7	18	3	3	1.7	1.7	1.3	1.3	79	79	4	4
Si	-	-	-	-	-	-	-	-	-	-	1	1	141	141	-	-	-	-	-	-
P	2	2	11.6	11.6	14.6	14.6	126	126	2	2	3	3	4.5	4.5	3.7	3.7	84	84	4	4
S		-		**20,000**		-		-		-	8	8	25,572	25,572	2,478	3,478	10	10	83	83
Cl		-		**45**		-		-		-	0	0	-	-	-	-	-	-	-	-
K	2	2	4.9	4.9	3.6	3.6	72	72	3	3	4	4	12.7	12.7	13.9	13.9	110	110	4	4
Ca	7	5	25.8	10.5	41.6	1.6	161	15	4	33	6	6	13.3	13.3	6.5	6.5	49	49	12	12
Sc	-	-	-	-	-	-	-	-	-	-	2	2	0.00530	0.00530	0.00014	0.00014	3	3	75	75
Ti	2	2	0.138	0.138	0.005	0.005	4	4	56	56	2	2	0.23	0.23	0.20	0.20	88	88	2	2
V		-		**28.19**		**0.40**		**1**		-		-		**390**		**10**		**3**		-
Cr	10	8	0.25	0.22	0.18	0.05	69	24	14	33	8	7	0.19	0.13	0.18	0.08	97	59	8	12
Mn	11	10	0.32	0.29	0.09	0.04	29	15	38	66	7	7	0.73	0.73	-	-	-	-	-	-
Fe	16	14	41.2	35.3	18.7	9.8	45	28	35	51	14	12	5.2	5.1	1.5	0.9	30	17	47	69
Co		-		**0.151**		**0.005**		**3**		-	5	5	0.65	0.65	0.07	0.07	10	10	49	49
Ni		-		**17.54**		**0.21**		**1**		-	22	19	49.9	50.2	2.8	1.9	6	4	395	504
Cu	13	12	0.45	0.37	0.35	0.21	79	58	17	21	8	8	0.20	0.20	0.14	0.14	70	70	11	11
Zn	9	8	4.11	3.14	3.05	0.94	74	30	12	27	5	5	0.52	0.52	0.16	0.16	32	32	16	16
Ga	2	2	0.021	0.021	0.003	0.003	12	12	16	16	4	4	0.0335	0.0335	0.0018	0.0018	6	6	73	73
Ge	2	2	0.010	0.010	0.002	0.002	22	22	9	9	4	4	0.0054	0.0054	0.0024	0.0024	44	44	9	9
As		-		**0.143**		**0.006**		**4**		-	5	5	0.18	0.18	0.04	0.04	22	22	22	22
Se		-		**0.102**		**0.004**		**4**		-	2	2	0.32	0.32	0.07	0.07	23	23	9	9
Rb	3	3	0.0055	0.0055	0.0012	0.0012	21	21	14	14	2	2	0.0013	0.0013	0.0006	0.0006	44	44	5	5
Sr	8	7	0.42	0.39	0.10	0.05	23	12	35	58	5	5	0.27	0.27	0.06	0.06	21	21	23	23
Y	-	-	-	-	-	-	-	-	-	-	4	4	0.028	0.028	0.010	0.010	36	36	11	11
Zr	3	3	0.009	0.009	0.004	0.004	48	48	6	6	7	7	0.054	0.054	0.046	0.046	86	86	8	8
Mo	11	9	0.136	0.105	0.080	0.023	59	22	19	41	12	12	0.28	0.28	0.06	0.06	20	20	59	59
Ru	-	-	-	-	-	-	-	-	-	-	1	1	0.000004	0.000004	-	-	-	-	-	-
Pd	-	-	-	-	-	-	-	-	-	-	1	1	0.00016	0.00016	-	-	-	-	-	-
Ag	2	2	0.05	0.05	0.07	0.07	141	141	1	1	0	0	-	-	-	-	-	-	-	-
Cd	4	4	0.0022	0.0022	0.0007	0.0007	30	30	13	13	2	2	0.0015	0.0015	0.0010	0.0010	66	66	3	3
Sn	1	1	0.011	0.011	-	-	-	-	-	-	1	1	0.081	0.081	-	-	-	-	-	-
Sb	4	4	0.009	0.009	0.004	0.004	49	49	8	8	3	3	0.0119	0.0119	0.0007	0.0007	6	6	50	50
Te	1	1	0.003	0.003	-	-	-	-	-	-	0	0	-	-	-	-	-	-	-	-
Cs	-	-	-	-	-	-	-	-	-	-	1	1	0.00008	0.00008	-	-	-	-	-	-
Ba		-		**1.8**		-		-		-	9	8	0.47	0.45	0.09	0.07	19	16	47	50

Table 6. *Cont.*

	NIST 1634c										NIST 8505									
	n	***n***	**Mean**	**Mean**	**SD (±)**	**SD (±)**	**RSD**	**RSD**	***n*/RSD**	***n*/RSD**	***n***	***n***	**Mean**	**Mean**	**SD (±)**	**SD (±)**	**RSD**	**RSD**	***n*/RSD**	***n*/RSD**
	No Filter	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**	**No Filter**	**2σ Filter**
			ppm	**ppm**	**ppm**	**ppm**	**%**	**%**	**%**	**%**			**ppm**	**ppm**	**ppm**	**ppm**	**%**	**%**	**%**	**%**
La	-	-	-	-	-	-	-	-	-	-	2	2	0.0134	0.0134	-	-	-	-	-	-
Ce	-	-	-	-	-	-	-	-	-	-	3	3	0.0291	0.0291	0.0063	0.0063	22	22	14	14
Pr	-	-	-	-	-	-	-	-	-	-	2	2	0.0041	0.0041	0.0011	0.0011	28	28	7	7
Nd	-	-	-	-	-	-	-	-	-	-	3	3	0.0188	0.0188	0.0043	0.0043	23	23	13	13
Sm	-	-	-	-	-	-	-	-	-	-	2	2	0.0057	0.0057	0.0018	0.0018	31	31	6	6
Eu	-	-	-	-	-	-	-	-	-	-	2	2	0.0017	0.0017	0.0006	0.0006	33	33	6	6
Gd	-	-	-	-	-	-	-	-	-	-	2	2	0.0074	0.0074	0.0021	0.0021	28	28	7	7
Tb	-	-	-	-	-	-	-	-	-	-	2	2	0.0013	0.0013	0.0004	0.0004	28	28	7	7
Dy	-	-	-	-	-	-	-	-	-	-	2	2	0.0076	0.0076	-	-	-	-	-	-
Ho	-	-	-	-	-	-	-	-	-	-	2	2	0.0016	0.0016	0.0004	0.0004	23	23	9	9
Er	-	-	-	-	-	-	-	-	-	-	2	2	0.0045	0.0045	0.0015	0.0015	33	33	6	6
Tm	-	-	-	-	-	-	-	-	-	-	2	2	0.0006	0.0006	0.00014	0.00014	24	24	8	8
Yb	-	-	-	-	-	-	-	-	-	-	2	2	0.0037	0.0037	0.0012	0.0012	33	33	6	6
Lu	-	-	-	-	-	-	-	-	-	-	2	2	0.0006	0.0006	0.00014	0.00014	24	24	8	8
Hf	-	-	-	-	-	-	-	-	-	-	1	1	0.0005	0.0005	-	-	-	-	-	-
Ta	-	-	-	-	-	-	-	-	-	-	1	1	0.00003	0.00003	-	-	-	-	-	-
Re	3	3	0.00156	0.00156	0.00017	0.00017	11	11	28	28	7	7	0.00243	0.00243	0.00030	0.00030	12	12	57	57
Os	1	1	0.00003	0.00003	-	-	-	-	-	-	7	7	0.00003	0.00003	0.000004	0.000004	12	12	56	56
Ir	-	-	-	-	-	-	-	-	-	-	1	1	0.00001	0.00001	-	-	-	-	-	-
Pt	-	-	-	-	-	-	-	-	-	-	1	1	0.00013	0.00013	-	-	-	-	-	-
Hg	1	1	0.12	0.12	-	-	-	-	-	-	0	0	-	-	-	-	-	-	-	-
Tl	1	1	0.003	0.003	-	-	-	-	-	-	0	0	-	-	-	-	-	-	-	-
Pb	13	12	0.36	0.33	0.16	0.13	45	38	29	31	3	3	0.04	0.04	0.04	0.04	91	91	3	3
Bi	2	2	0.0024	0.0024	0.0013	0.0013	53	53	4	4	0	0	-	-	-	-	-	-	-	-
Th	-	-	-	-	-	-	-	-	-	-	2	2	0.0046	0.0046	0.0025	0.0025	55	55	4	4
U	6	6	0.0034	0.0034	0.0015	0.0015	44	44	14	14	2	2	0.0006	0.0006	0.0003	0.0003	47	47	4	4

Note: Certificate values—in Bold; *n*—number of values.

More than 1/3 of the elements (e.g., Mn, Fe, Co, As, Se, Sr, Mo, Ba, Re, Os, Ce, Lu) in the updated NIST 8505 compilation have relatively low scatter (RSD $\leq$ 25%, Table 6). Among these, V, Ni, Ga, Sb, H, C, and Sc exhibit the lowest variance (4–6% RSD). The rest of the elements show larger variance, with few elements having RSD > 90%.

In total, 39 elements for NIST 1634c and 63 elements for NIST 8505 were included in our compilation. The mean values for ~2/3 of the elements for NIST 1634c and ~1/3 of the elements for NIST 8505 are based on more than three reported values (both published data and this study). More than half of the elements in NIST 1634c (22 elements) and more than 1/3 of the elements in NIST 8505 (24 elements) exhibit relatively low scatter (RSD $\leq$ 25%, Table 6), with the lowest variance among the widely used elements covered in the certificates, like V, Ni, and Co, (RSD $\leq$ 10%, and usually within 5%).

3.6. The Effects of Incomplete Digestion on Key Trace Metal Ratios

Trace metal ratios are commonly used to examine oil-to-oil and oil-to-rock correlations due to their relatively constant values in crude oils and related natural petroleum products at variable degrees of diagenetic and alteration processing in the reservoir (e.g., [3,4,97]). For example, Co/Ni and V/Ni are indicative for the depositional environment of the source rocks (terrestrial vs. marine and mixed-source organic matter) (e.g., [5,98]), whereas due to their redox sensitivity, V, Ni, Co, Mo, and Cu are used as paleoredox proxies (e.g., [99,100]). In particular, V/Ni and V/(V + Ni) ratios are widely used as markers for source-rock type, depositional conditions and crude oil maturity. Their application is based on empirical observations that even though natural processes such as crude oil expulsion, migration or entrapment can change the concentrations of these two metals, they are affected to a similar extent, and their ratios remain largely unchanged [3]. However, the effects of incomplete sample digestion on those ratios have not been assessed. Here, we use our results on the efficiency of the four different digestion procedures employed in this study (Table 7) to evaluate if, and how V/Ni, V/(V + Ni), and other ratios are affected by incomplete digestion.

Table 7. The match (in %) between the measured elemental ratios and ratios calculated from certificate values (and selected mean published values in the case of NIST 8505).

Ratios	V/Ni	V/(V + Ni)	Co/Ni	Co/V	As/V	As/Ni	As/Co	As/Ba	Ba/V	Ba/Ni	Co/Ba
NIST 1634c											
HPD	**97**	**99**	74	76	44	43	58	**84**	52	51	145
MD-C1	**90**	**96**	**80**	**90**	78	70	**87**	**117**	67	60	135
MD-C2	**100**	**100**	**82**	**82**	79	79	**96**	**101**	78	78	**105**
MD-C3	**100**	**100**	**85**	**85**	77	77	**90**	**109**	70	70	121
MPV	**102**	**101**	**95**	**94**	**102**	**104**	**110**	**125**	**82**	**83**	**114**
NIST 8505											
MD-C1	**104**	**100**	**91**	**87**	67	70	77	56	**119**	124	73
MD-C2	**102**	**100**	**93**	**91**	63	64	69	50	126	128	73
MD-C3	**107**	**101**	**95**	**89**	66	71	75	51	130	139	68

Bold numbers: ±20% match; gray boxes: ±30% match; symbols are as in Table 3.

3.6.1. Trace Element Ratios for NIST 1634c

The match between measured V/Ni and V/(V + Ni) ratios and calculated certified ratios is excellent (100%) for two- and three-cycle microwave digestion, followed by hotplate digestion (97–99%), which are characterized by recoveries for both elements between 101% and 111% (Table 5, Figure 5A). For one-cycle microwave digestion, characterized by relatively lower recoveries for V (82%) and Ni (91%), the match between measured V/Ni and V/(V + Ni) ratios and calculated certified ratios is also lower: 90% for V/Ni and 96% for V/(V + Ni) (Table 7). Despite these lower ratios, a 90% accuracy of the V/Ni ratios in

C1 digestion is considered sufficient for the purpose of discriminating between natural variations in V/Ni ratios among different crude oils, which often vary orders of magnitude. For example, a compilation of V/Ni ratios in crude oils from Venezuela shows a range from near zero up to ca. 12; these V/Ni ratios increase systematically from the Barinas-Apure Basin to the Eastern Basin to the Maracaibo Basin [7].

Overall, our results show that even at a mildly insufficient degree of digestion, V and Ni are similarly affected (both have lower recoveries), likely because they occupy similar classes of organic compounds (e.g., metalloporphyrins; [4,101,102]). As a result, their ratios remain relatively close to those of fully digested samples (e.g., C2 and C3 digestion), either because all metalloporphyrins were digested (unlike other types of organic compounds) or because V and Ni are proportionally distributed between the digested and undigested portions of metalloporphyrins in the partially digested samples.

Ratios including V and Ni with other elements provided in the certificate like Co, As, and Ba, demonstrated best matches in C2 microwave-digested samples (78–105%) followed by C3 samples (70–121%), whereas C1 and HPD samples provided larger ranges of 60–135% and 43–145%, respectively (typically << 90%). This relationship indicates that Co, As and Ba likely occupy different organic compounds compared with V and Ni. When we compare elemental ratios from the updated NIST 1634c compilation with the ratios calculated from certificate values, we obtained best matches for V/(V + Ni) and V/Ni (101–102%). Ratios of Co and As with V and Ni are close to the calculated certified ratios (94–104%), whereas those of Ba with V and Ni are lower (82–83%, Table 7). These overall good matches suggest that the updated NIST 1634c compilation accurately represents the "true" trace metal ratios of V, Ni, Co and As of this fuel oil. Although this conclusion cannot be unconditionally extended to include all other trace metal ratios between non-certified elements, it does provide some positive indications for the overall validity of the updated NIST 1634c compilation for the true trace metal ratios of this material.

3.6.2. Trace Element Ratios for NIST 8505

Unlike NIST 1634c, NIST 8505 crude oil has only one element (V) with a specified concentration in its certificate, and hence, we cannot evaluate the effect of incomplete digestion on the trace metal ratios between certified elements. However, when we compared measured ratios for this material with their respective ratios obtained from the mean published trace metal concentrations for NIST 8505, we note somewhat similar relations as for NIST 1634c (Table 7). In NIST 8505, all three microwave digestion methods show excellent match for V/Ni (102–107%) and particularly V/(V + Ni) ratios (100–101%), followed by Co/Ni and Co/V (87–95%). Similarly to in NIST 1634c, lower ratios of As with V, Ni, Co, and Ba were observed in all three MD procedures (50–77%). In contrast to NIST 1634c, the NIST 8505 ratios of Ba with V and Ni are higher than the expected ratios from the mean published values (119–139%, Table 7).

In summary, for both reference materials in all digestion groups, V/Ni and V/(V + Ni) ratios were within 90–107% of the certified ratios (NIST 1634c) or expected ratios based on the mean published values (for NIST 8505), with the best overlap (100–107%) for the C2 and C3 MD procedures. Importantly, V/Ni and V/(V + Ni) ratios remained sufficiently close to the certified or expected values even during procedures with incomplete sample decomposition, such as C1 microwave digestion (and HPD-S, see Supplementary Table S7), which have relatively lower recoveries for V and Ni (Figure 5A,B; Table 5).

4. Conclusions

In this study, we tested four different methods for acid digestion of petroleum samples: one by hotplate digestion and three by microwave digestion (one, two, and three digestion

cycles). The trace metal contents of two petroleum reference materials digested by the above procedures were analyzed by ICP-MS and compared with the limited number of trace metals in the certificates of these materials to evaluate the efficiency of the digestion procedures. Certificate-based recovery rates for the studied samples yielded the best overall results for two and three cycles of microwave digestion, whereas we show that the commonly used one-cycle digestion procedure is insufficient for complete decomposition of the studied petroleum samples. Thus, our results highlight the need for a more aggressive and prolonged acid digestion of petroleum samples than is usually recommended by manufacturers of microwave equipment for acid digestion.

These conclusions are further reinforced by the comparison of our results with the mean published values for elements not included in the certificates (i.e., most trace elements), which were obtained from a newly presented comprehensive compilation of published trace element contents for the two studied reference materials. Similar to the certificate-based comparison, two and three cycles of microwave digestion of NIST 1634c and NIST 8505 seem to provide the optimum results. Integrating the recoveries for both certified and non-certified elements, and taking into account secondary considerations such as the analytical scatter, the visual appearance of the digested solutions, and the digestion recipe (amount of acids added and time), we favor either two- or three-cycle microwave digestion for the decomposition of crude oil and related products.

The hotplate digestion yielded positive results for most of the certified elements. Recoveries for the remaining elements are highly variable, which may reflect the limitations of using non-certified mean published values as a baseline for comparison, combined with some degree of contamination and/or losses due to extended digestion-evaporation cycles over a long period of time (~21 days for the entire procedure). Therefore, we consider efficient hotplate digestion of petroleum samples in closed vials achievable, provided further improvements of the procedure are implemented to shorten its duration and reduce the risk of contamination and losses.

The newly presented compilation of published trace element data for the two reference materials, augmented with new results for the most efficient digestion procedures from this study, provides a solid basis for a thorough characterization of the elemental composition of NIST 8505 and NIST 1634c reference materials. Furthermore, the mean updated compositions can be used as a non-certified reference database for evaluating analytical results in future studies on petroleum products and can further be updated by the acquisition of new quality data.

Finally, we explore the effects of incomplete digestion on the most widely used trace metal ratios in petroleum geology. We show that the V/Ni and V/(V + Ni) ratios typically applied for oil-to-oil and oil-to-source rock correlations were little affected by incomplete oil digestion. The ratios remained relatively constant and close to the calculated certified ratios among all tested digestion procedures for NIST 1634c, and nearly identical to the expected ratios in NIST 8505. This suggests that the two elements are hosted in similar-to-identical types of molecules within the complex matrix of the crude oil, and their ratios are thus preserved even at insufficient degrees of sample digestion. Therefore, our results reinforce the validity of most of the reported V/Ni and V/(V + Ni) ratios even in cases where the concentrations of the two elements may be underestimated due to incomplete sample digestion.

Overall, our study offers an improved protocol for acid digestion of petroleum samples and provides updated compositions of the NIST 1634c and NIST 8505 reference materials, which can be used for improving the quality of future trace element studies on petroleum and the interpretation of trace element contents and ratios in crude oil and related products. Further research directed towards more precise analyses for elements with relatively large

scatter (e.g., Be, P, K, Cu, Zr, Zg, Sb, Bi, Pb, U for NIST 1634c, and Li, B, Al, K, Ca, Na, P, Ti, Cr, Cu, Zr, Cd, Pb, Th, U for NIST 8505) and other underreported elements can further characterize the trace metal composition of community-used trace metal petroleum standards.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/geosciences16020074/s1, Table S1: ICP-MS operating conditions; Table S2: Multi-element calibration standard solutions; Table S3: Detailed characteristics of the digested and diluted samples for NIST SRM 1634c and NIST RM 8505; Table S4: Compilation of published data for NIST SRM 1634c; Table S5: Compilation of published data for NIST RM 8505; Table S6: Trace element recoveries for all studied samples according to certificate values and mean published values for NIST 1634c and NIST 8505; Table S7: Ratios of certificate-covered elements for NIST 1634c and all followed by the same ratios for NIST 8505 in all digestion groups.

Author Contributions: Conceptualization, S.G.; Methodology, S.G., E.R., L.B. and G.M.; Validation, S.G., E.R. and L.B.; Formal analysis, E.R., L.B. and G.M.; Investigation, L.B., E.R. and S.G.; Resources, E.R. and S.G.; Data curation, E.R. and L.B.; Writing—original draft preparation, E.R. and L.B.; Writing—review and editing, L.B. and S.G.; Visualization, E.R., L.B. and S.G.; Supervision, L.B. and S.G.; Project administration, S.G., and E.R.; Funding acquisition, S.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Bulgarian National Science Fund, project number КП-06-ДВ/6.

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

Acknowledgments: We thank Valentina Lyubomirova, Elitsa Stefanova and Valentin Ganev for their help with various aspects of the analytical work.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AES/OES	Optical or Atomic Emission Spectrometry
AV	Axially Viewed
CID	Charge Injection Device
CS	Confidence Score
DRC	Dynamic Reaction Cell
ED	Energy Dispersive
ET	Electrothermal
F-AAS	Flame Atomic Absorption Spectrometry
GF	Graphite Furnace
HG	Hydride Generation
HPA-S	High-Pressure Asher System
HPD	Hotplate Acid Digestion
HR-CS	High-Resolution Continuum Source
IC	Ion Chromatography System
ICP	Inductively Coupled-Plasma Mass Spectrometry
LA	Laser Ablation
N-TIMS	Negative Thermal-Ionization Mass Spectrometry
MC	Multicollector
MD	Microwave Acid Digestion

MIC	Microwave-Induced Combustion
MFN	Micro-Flow Nebulizer
MP	Microwave-Induced Plasma
MPV	Mean Published Value
MS	Mass Spectrometry
NIST	National Institute of Standards and Technology
PDC	Pressurized Digestion Cavity
QQQ	Triple Quadrupole
RM	Research Material
SF	Sector Field
SRC	Single Reaction Chamber
SRM	Standard Reference Material
TAB	Total Analytical Blank
USN	Ultrasonic Nebulization
XRF	X-Ray Fluorescence

References

1. Tissot, B.; Welte, D.H. *Petroleum Formation and Occurrence*, 2nd ed.; Springer: Berlin/Heidelberg, Germany, 1984; p. 720. [CrossRef]
2. Hunt, J.M. *Petroleum Geochemistry and Geology*, 2nd ed.; W. H. Freeman and Company: New York, NY, USA, 1996; p. 763. [CrossRef]
3. Lewan, M.D. Factors controlling the proportionality of vanadium to nickel in crude oils. *Geochim. Cosmochim. Acta* **1984**, *48*, 2231–2238. [CrossRef]
4. Barwise, A.J.G. Role of nickel and vanadium in petroleum classification. *Energy Fuels* **1990**, *4*, 647–652. [CrossRef]
5. Galarraga, F.; Reategui, K.; Martinez, A.; Martinez, M.; Llamas, J.F.; Marquez, G. V/Ni ratio as a parameter in palaeoenvironmental characterisation of nonmature medium-crude oils from several Latin American basins. *J. Pet. Sci. Eng.* **2008**, *61*, 9–14. [CrossRef]
6. Georgiev, S.V.; Stein, H.J.; Hannah, J.L.; Yang, G.; Markey, R.J.; Dons, C.E.; Pedersen, J.H.; Di Primio, R. Comprehensive evolution of a petroleum system in absolute time: The example of Brynhild Norwegian North Sea. *Chem. Geol.* **2019**, *522*, 260–282. [CrossRef]
7. Hurtig, N.C.; Georgiev, S.V.; Zimmerman, A.; Yang, G.; Goswami, V.; Hannah, J.L.; Stein, H.J. Re-Os geochronology for the NIST RM 8505 crude oil: The importance of analytical protocol and uncertainty. *Chem. Geol.* **2020**, *539*, 119381. [CrossRef]
8. Georgiev, S.V.; Botoucharov, N.; Morin, G.; Raeva, E.; Marinovska, E.; Lyubomirova, V.; Bidzhova, L. Vanadium, Ni, S and Hg contents in Bulgarian crude oils: Genetic and environmental implications. *Rev. Bulg. Geol. Soc.* **2024**, *85*, 105–108. [CrossRef]
9. Georgiev, S.V.; Stein, H.J.; Hannah, J.L.; Galimberti, R.; Nali, M.; Yang, G.; Zimmerman, A. Re–Os dating of maltenes and asphaltenes within single samples of crude oil. *Geochim. Cosmochim. Acta* **2016**, *179*, 53–75. [CrossRef]
10. Selby, D.; Creaser, R.A.; Fowler, M.G. Re–Os elemental and isotopic systematics in crude oils. *Geochim. Cosmochim. Acta* **2007**, *71*, 378–386. [CrossRef]
11. Skrbic, B.; Novakovic, J.; Miljevic, N. Mobility of heavy metals originating from bombing of industrial sites. *J. Environ. Sci. Health Part A* **2002**, *37*, 7–16. [CrossRef]
12. Kreider, R.E. Identification of oil leaks and spills. In *International Oil Spill Conference*; American Petroleum Institute: Washington, DC, USA, 1971; Volume 1971, pp. 119–124. [CrossRef]
13. Abu-Elgheit, M.A. Oil spill source identification by infrared, gas chromatographic, and trace metal analyses. *Environ. Int.* **1982**, *7*, 305–308. [CrossRef]
14. Boehm, P.D.; Douglas, G.S.; Burns, W.A.; Mankiewicz, P.J.; Page, D.S.; Bence, A.E. Application of petroleum hydrocarbon chemical fingerprinting and allocation techniques after the Exxon Valdez oil spill. *Mar. Pollut. Bull.* **1997**, *34*, 599–613. [CrossRef]
15. Liu, X. Advantages of multidimensional chemical fingerprinting in identifying the source of marine oil spills in Bohai Bay, China. In *Oil Spill Environmental Forensics Case Studies*; Butterworth-Heinemann: Portsmouth, NH, USA, 2018; pp. 239–253. [CrossRef]
16. Hegazi, A.H. Utilization of trace metals in source diagnosing of tar balls from the Mediterranean city of Alexandria, Egypt. *Pet. Sci. Technol.* **2009**, *27*, 386–395. [CrossRef]
17. Hazrati, M.; Taleshi, M.S.; Chaichi, M.J. Characterization of trace metals in source identification of tar balls deposited along the southern coast of the Caspian Sea. *Pet. Sci. Technol.* **2017**, *35*, 710–717. [CrossRef]
18. Scarlett, A.G.; Holman, A.I.; Georgiev, S.V.; Stein, H.J.; Summons, R.E.; Grice, K. Multi-spectroscopic and elemental characterization of southern Australian asphaltites. *Org. Geochem.* **2019**, *133*, 77–91. [CrossRef]
19. Fabec, J.L.; Ruschak, M.L. Determination of nickel, vanadium, and sulfur in crudes and heavy crude fractions by inductively coupled argon plasma atomic emission spectrometry and flame atomic absorption spectrometry. *Anal. Chem.* **1985**, *57*, 1853–1863. [CrossRef]

20. Reynolds, J.G. Nickel in petroleum refining. *Pet. Sci. Technol.* **2001**, *19*, 979–1007. [CrossRef]
21. Speight, J.G. *Handbook of Petroleum Refining*; CRC Press: Boca Raton, FL, USA, 2016; p. 725. [CrossRef]
22. Hwang, J.D.; Horton, M.; Leong, D. The use of microwave digestion and ICP to determine elements in petroleum samples. *J. ASTM Int.* **2005**, *2*, 12967. [CrossRef]
23. Dreyfus, S.; Pecheyran, C.; Magnier, C.; Prinzhofer, A.; Lienemann, C.P.; Donard, O.F.X. Direct trace and ultra-trace metals determination in crude oil and fractions by inductively coupled plasma mass spectrometry. *J. ASTM Int.* **2005**, *2*, 12969. [CrossRef]
24. Doyle, A.; Saavedra, A.; Tristao, M.L.B.; Aucelio, R.Q. Determination of S, Ca, Fe, Ni and V in crude oil by energy dispersive X-ray fluorescence spectrometry using direct sampling on paper substrate. *Fuel* **2015**, *162*, 39–46. [CrossRef]
25. Damin, I.C.; Vale, M.G.R.; Silva, M.M.; Welz, B.; Lepri, F.G.; Dos Santos, W.N.; Ferreira, S.L. Palladium as chemical modifier for the stabilization of volatile nickel and vanadium compounds in crude oil using graphite furnace atomic absorption spectrometry. *J. Anal. At. Spectrom.* **2005**, *20*, 1332–1336. [CrossRef]
26. De Albuquerque, F.I.; Duyck, C.B.; Fonseca, T.C.O.; Saint'Pierre, T.D. Determination of As and Se in crude oil diluted in xylene by inductively coupled plasma mass spectrometry using a dynamic reaction cell for interference correction on ^{80}Se. *Spectrochim. Acta Part B At. Spectrosc.* **2012**, *71*, 112–116. [CrossRef]
27. Lepri, F.G.; Welz, B.; Borges, D.L.; Silva, A.F.; Vale, M.G.R.; Heitmann, U. Speciation analysis of volatile and non-volatile vanadium compounds in Brazilian crude oils using high-resolution continuum source graphite furnace atomic absorption spectrometry. *Anal. Chim. Acta* **2006**, *558*, 195–200. [CrossRef]
28. Casey, J.; Gao, Y.; Yang, W.; Thomas, R. New approaches in sample preparation and precise multielement analysis of crude oils and refined petroleum products using single-reaction-chamber microwave digestion and triple-quadrupole ICP-MS. *Spectroscopy* **2016**, *31*, 11–22. Available online: https://www.researchgate.net/publication/310447142 (accessed on 30 October 2017).
29. Yang, W.; Casey, J.F.; Gao, Y. A new sample preparation method for crude or fuel oils by mineralization utilizing single reaction chamber microwave for broader multi-element analysis by ICP techniques. *Fuel* **2017**, *206*, 64–79. [CrossRef]
30. Wondimu, T.; Goessler, W. Comparison of closed-pressurized and open-refluxed vessel digestion systems for trace elements in the residual fuel oil reference material (SRM 1634c). *Bull. Chem. Soc. Ethiop.* **2000**, *14*, 99–113. [CrossRef]
31. Amoli, H.S.; Porgam, A.; Sadr, Z.B.; Mohanazadeh, F. Analysis of metal ions in crude oil by reversed-phase high performance liquid chromatography using short column. *J. Chromatogr. A* **2006**, *1118*, 82–84. [CrossRef]
32. Flores, E.M.; Barin, J.S.; Mesko, M.F.; Knapp, G. Sample preparation techniques based on combustion reactions in closed vessels—A brief overview and recent applications. *Spectrochim. Acta Part B At. Spectrosc.* **2007**, *62*, 1051–1064. [CrossRef]
33. Mello, P.A.; Pereira, J.S.; Mesko, M.F.; Barin, J.S.; Flores, E.M. Sample preparation methods for subsequent determination of metals and non-metals in crude oil—A review. *Anal. Chim. Acta* **2012**, *746*, 15–36. [CrossRef] [PubMed]
34. Ventura, G.T.; Gall, L.; Siebert, C.; Prytulak, J.; Szatmari, P.; Hürlimann, M.; Halliday, A.N. The stable isotope composition of vanadium; nickel; and molybdenum in crude oils. *Appl. Geochem.* **2015**, *59*, 104–117. [CrossRef]
35. Nelson, J.; Gilleland, G.; Poirier, L.; Leong, D.; Hajdu, P.; Lopez-Linares, F. *Direct Multi-Elemental Analysis of Crude Oils Using the Agilent 4200/4210 Microwave Plasma-Atomic Emission Spectrometer*; Agilent Technologies: Santa Clara, CA, USA, 2016. Available online: https://www.agilent.com/cs/library/applications/5991-7104EN.pdf (accessed on 1 September 2016).
36. Poirier, L.; Nelson, J.; Gilleland, G.; Wall, S.; Berhane, L.; Lopez-Linares, F. Comparison of Preparation Methods for the Determination of Metals in Petroleum Fractions (1000 °F+) by Microwave Plasma Atomic Emission Spectroscopy. *Energy Fuels* **2017**, *31*, 7809–7815. [CrossRef]
37. Poirier, L.; Nelson, J.; Gilleland, G.; Wall, S.; Berhane, L.; Lopez-Linares, F. *Determination of Metals in Petroleum Fractions Using MP-AES*; Agilent Technologies—Energy and Chemicals: Santa Clara, CA, USA, 2018; Volume 6. Available online: https://www.agilent.com/cs/library/applications/5991-9122EN_metals_petrol_mp-aes_application.pdf (accessed on 21 March 2018).
38. Nelson, J.; Singha, S.; Drvodelic, N. *High-Throughput Multi-Elemental Analysis of Crude Oil*; Agilent Technologies—Petrochemicals: Santa Clara, CA, USA, 2019; Volume 7. Available online: https://www.agilent.com/cs/library/applications/application_crude_oil_icp-oes_5110_5994-1583en_us_agilent.pdf (accessed on 17 December 2019).
39. De Souza, J.R.; Dos Santos, E.F.; Duyck, C.B.; Saint'Pierre, T.D. Comparison of parallel flow and concentric micronebulizers for elemental determination in lubricant oil; residual fuel oil and biodiesel by Inductively Coupled Plasma Optical Emission Spectrometry. *Spectrochim. Acta Part B At. Spectrosc.* **2011**, *66*, 356–361. [CrossRef]
40. Poirier, L.; Nelson, J.; Leong, D.; Berhane, L.; Hajdu, P.; Lopez-Linares, F. Application of ICP-MS and ICP-OES on the Determination of Nickel, Vanadium, Iron, and Calcium in Petroleum Crude Oils via Direct Dilution. *Energy Fuels* **2016**, *30*, 3783–3790. [CrossRef]
41. Nelson, J.; McCurdy, E. *Multi-Element Analysis of Petroleum Crude Oils Using an Agilent 7900 ICP-MS*; Agilent Technologies—Energy and Fuels: Santa Clara, CA, USA, 2017; Volume 7. Available online: https://www.researchgate.net/publication/320455738 (accessed on 17 October 2017).

42. De Souza, J.R.; Duyck, C.B.; Fonseca, T.C.; Saint'Pierre, T.D. Multielemental determination in oil matrices diluted in xylene by ICP-MS with a dynamic reaction cell employing methane as reaction gas for solving specific interferences. *J. Anal. At. Spectrom.* **2012**, *27*, 1280–1286. [CrossRef]
43. Surekar, B.; Kutscher, D. *Analytical Testing of Trace Elements in Refinery Products Using a Robust ICP-MS Approach; AN44465-EN 0720S*; Thermo Fisher Scientific Inc.: Waltham, MA, USA, 2020; Volume 9. Available online: https://icpms.labrulez.com/paper/27403 (accessed on 29 January 2026).
44. Todoli-Carbonell, M.; Perez-Ramirez, R.; Coquet, T.; Chainet, F.; Lacoue-Negre, M.; Sanchez-Romero, R. Cutting-edge arsenic quantification in pyrolysis oils: Evaluation of a high temperature torch integrated sample introduction system (hTISIS) combined with an ICP-MS/MS. *J. Anal. At. Spectrom.* **2025**, *40*, 1343–1352. [CrossRef]
45. Martinez, S.; Morineau, L.; Fernandes, J.; Chainet, F. Novel method for chlorine determination in biofuel lipid feedstock by coupling a total sample introduction system (hTISIS) to an inductively coupled plasma tandem mass spectrometry (ICP-MS/MS). *Anal. Chim. Acta* **2024**, *1301*, 342414. [CrossRef]
46. Pohl, P.; Vorapalawut, N.; Bouyssiere, B.; Carrier, H.; Lobinski, R. Direct multi-element analysis of crude oils and gas condensates by double-focusing sector field inductively coupled plasma mass spectrometry (ICP MS). *J. Anal. At. Spectrom.* **2010**, *25*, 704–709. [CrossRef]
47. Gajdosechova, Z.; Mester, Z.; Pagliano, E. A rapid and sensitive method for the determination of inorganic chloride in oil samples. *Anal. Chim. Acta* **2019**, *1064*, 40–46. [CrossRef]
48. Tittarelli, P.; Priola, M.; Ricchiuto, S.; Katskov, D.A.; Ngobeni, P. Fuel analysis by filter furnace electrothermal atomic absorption spectrometry. *J. ASTM Int.* **2005**, *2*, 1–12. [CrossRef]
49. Kowalewska, Z. Direct determination of nickel in xylene solutions of raw material for catalytic cracking with application of graphite furnace atomic absorption spectrometry. *Anal. Methods* **2013**, *5*, 192–201. [CrossRef]
50. Duyck, C.; Miekeley, N.; Fonseca, T.C.; Szatmari, P.; Santos Neto, E.V.D. Trace element distributions in biodegraded crude oils and fractions from the Potiguar Basin, Brazil. *J. Braz. Chem. Soc.* **2008**, *19*, 978–986. [CrossRef]
51. Duyck, C.; Miekeley, N.; Da Silveira, C.L.P.; Szatmari, P. Trace element determination in crude oil and its fractions by inductively coupled plasma mass spectrometry using ultrasonic nebulization of toluene solutions. *Spectrochim. Acta Part B At. Spectrosc.* **2002**, *57*, 1979–1990. [CrossRef]
52. Meeravali, N.N.; Kumar, S.J. The utility of a W–Ir permanent chemical modifier for the determination of Ni and V in emulsified fuel oils and naphtha by transverse heated electrothermal atomic absorption spectrometer. *J. Anal. At. Spectrom.* **2001**, *16*, 527–532. [CrossRef]
53. Oliveira, I.K.S.; Medeiros, R.L.S.; Silva, D.R.; Maranhao, T.A. Determination of Chlorine in Crude Oil Emulsified via the MgCl Molecule by HR-CS MAS. *J. Braz. Chem. Soc.* **2018**, *29*, 571–578. [CrossRef]
54. Quadros, D.P.; Chaves, E.S.; Lepri, F.G.; Borges, D.L.; Welz, B.; Becker-Ross, H.; Curtius, A.J. Evaluation of Brazilian and Venezuelan crude oil samples by means of the simultaneous determination of Ni and V as their total and non-volatile fractions using high-resolution continuum source graphite furnace atomic absorption spectrometry. *Energy Fuels* **2010**, *24*, 5907–5911. [CrossRef]
55. Carballo-Paradelo, S.; Soto-Ferreiro, R.M.; Amor-Pastoriza, S.; Carlosena-Zubieta, A.; Fernandez-Fernandez, E.; Muniategui-Lorenzo, S.; Lopez-Mahia, P.; Prada-Rodriguez, D. Direct determination of V, Ni, and Co in emulsified fuel oil samples by electrothermal atomic absorption spectrometry (ETAAS). *At. Spectrosc.* **2009**, *30*, 129–138. Available online: https://www.at-spectrosc.com/as/article/issue/2009_30_4 (accessed on 29 January 2026).
56. Luz, M.S.; Nascimento, A.N.; Oliveira, P.V. Fast emulsion-based method for simultaneous determination of Co, Cu, Pb, and Se in crude oil, gasoline and diesel by graphite furnace atomic absorption spectrometry. *Talanta* **2013**, *115*, 409–413. [CrossRef] [PubMed]
57. Amorim, F.A.C.; Lima, D.C.; Amaro, J.A.; Vale, M.G.R.; Ferreira, S.L. Methods for vanadium determination in fuel oil by GF AAS with microemulsification and acid digestion sampling. *J. Braz. Chem. Soc.* **2007**, *18*, 1566–1570. [CrossRef]
58. De Souza, R.M.; Meliande, A.L.; Da Silveira, C.L.; Aucelio, R.Q. Determination of Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr and Co in crude oil using inductively coupled plasma optical emission spectrometry and sample introduction as detergentless microemulsions. *Microchem. J.* **2006**, *82*, 137–141. [CrossRef]
59. Vieira, L.V.; Marchezi, T.T.B.; De Castro, E.V.R.; Brandao, G.P.; Carneiro, M.T.W.D. Metals determination in crude oil by inductively coupled plasma optical emission spectrometry using nanoemulsification as sample preparation. *Fuel* **2019**, *244*, 352–358. [CrossRef]
60. Seeger, T.S.; Machado, E.Q.; Flores, E.M.; Mello, P.A.; Duarte, F.A. Direct sampling graphite furnace atomic absorption spectrometry-feasibility of Na and K determination in desalted crude oil. *Spectrochim. Acta Part B At. Spectrosc.* **2018**, *141*, 28–33. [CrossRef]
61. Seeger, T.S.; Muller, E.I.; Mesko, M.F.; Duarte, F.A. Magnesium and calcium determination in desalted crude oil by direct sampling graphite furnace atomic absorption spectrometry. *Fuel* **2019**, *236*, 1483–1488. [CrossRef]

62. Brandao, G.P.; De Campos, R.C.; De Castro, E.V.R.; De Jesus, H.C. Determination of copper, iron and vanadium in petroleum by direct sampling electrothermal atomic absorption spectrometry. *Spectrochim. Acta Part B At. Spectrosc.* **2007**, *62*, 962–969. [CrossRef]
63. Polidorio, D.I.; Naozuka, J.; Vieira, E.C.; Oliveira, P.V. Application of solid sampling device for direct determination of chromium and nickel in lubricating oils by graphite furnace atomic absorption spectrometry. *Anal. Lett.* **2008**, *41*, 1547–1554. [CrossRef]
64. Silva, M.M.; Damin, I.C.; Vale, M.G.R.; Welz, B. Feasibility of using solid sampling graphite furnace atomic absorption spectrometry for speciation analysis of volatile and non-volatile compounds of nickel and vanadium in crude oil. *Talanta* **2007**, *71*, 1877–1885. [CrossRef] [PubMed]
65. Brandao, G.P.; De Campos, R.C.; De Castro, E.V.R.; De Jesus, H.C. Direct determination of nickel in petroleum by solid sampling–graphite furnace atomic absorption spectrometry. *Anal. Bioanal. Chem.* **2006**, *386*, 2249–2253. [CrossRef] [PubMed]
66. Dittert, I.M.; Silva, J.S.; Araujo, R.G.; Curtius, A.J.; Welz, B.; Becker-Ross, H. Direct and simultaneous determination of Cr and Fe in crude oil using high-resolution continuum source graphite furnace atomic absorption spectrometry. *Spectrochim. Acta Part B At. Spectrosc.* **2009**, *64*, 537–543. [CrossRef]
67. DiMarzio, J.M.; Georgiev, S.V.; Stein, H.J.; Hannah, J.L. Residency of rhenium and osmium in a heavy crude oil. *Geochim. Cosmochim. Acta* **2018**, *220*, 180–200. [CrossRef]
68. Cussen, D.L.; Hensman, C.E. *Determination of Mercury and Other Trace Metals in Hydrocarbons Using the Anton-Paar High Pressure Asher (HPA)*; Frontier Geosciences Inc. (FGI): Seattle, DC, USA, 2011. Available online: https://coilink.org/20.500.12592/7gq4yxq (accessed on 21 April 2006).
69. Ricard, E.; Pecheyran, C.; Sanabria Ortega, G.; Prinzhofer, A.; Donard, O.F. Direct analysis of trace elements in crude oils by high-repetition-rate femtosecond laser ablation coupled to ICPMS detection. *Anal. Bioanal. Chem.* **2011**, *399*, 2153–2165. [CrossRef]
70. Walkner, C.; Gratzer, R.; Meisel, T.; Bokhari, S.N.H. Multi-element analysis of crude oils using ICP-QQQ-MS. *Org. Geochem.* **2017**, *103*, 22–30. [CrossRef]
71. Ortega, G.S.; Pécheyran, C.; Hudin, G.; Marosits, E.; Donard, O.F. Different approaches of crude oil mineralisation for trace metal analysis by ICPMS. *Microchem. J.* **2013**, *106*, 250–254. [CrossRef]
72. Pereira, J.S.; Moraes, D.P.; Antes, F.G.; Diehl, L.O.; Santos, M.F.; Guimaraes, R.C.; Fonseca, T.C.; Dressler, V.L.; Flores, E.M. Determination of metals and metalloids in light and heavy crude oil by ICP-MS after digestion by microwave-induced combustion. *Microchem. J.* **2010**, *96*, 4–11. [CrossRef]
73. Mello, P.D.A.; Pereira, J.S.F.; De Moraes, D.P.; Dressler, V.L.; De Moraes Flores, E.M.; Knapp, G. Nickel, vanadium and sulfur determination by inductively coupled plasma optical emission spectrometry in crude oil distillation residues after microwave-induced combustion. *J. Anal. At. Spectrom.* **2009**, *24*, 911–916. [CrossRef]
74. Pereira, J.S.; Mello, P.A.; Moraes, D.P.; Duarte, F.A.; Dressler, V.L.; Knapp, G.; Flores, E.M. Chlorine and sulfur determination in extra-heavy crude oil by inductively coupled plasma optical emission spectrometry after microwave-induced combustion. *Spectrochim. Acta Part B At. Spectrosc.* **2009**, *64*, 554–558. [CrossRef]
75. Dos Anjos, S.L.; Alves, J.C.; Soares, S.A.R.; Araujo, R.G.; De Oliveira, O.M.; Queiroz, A.F.; Ferreira, S.L. Multivariate optimization of a procedure employing microwave-assisted digestion for the determination of nickel and vanadium in crude oil by ICP OES. *Talanta* **2018**, *178*, 842–846. [CrossRef]
76. Nascimento, A.N.D.; Naozuka, J.; Oliveira, P.V.D. Closed-vessel microwave-assisted digestion using a diluted oxidant mixture for trace element determination in petrochemical samples by axially-viewed ICP OES. *Braz. J. Anal. Chem.* **2011**, *1*, 131–135. Available online: https://bv.fapesp.br/en/publicacao/243092/ (accessed on 20 September 2011).
77. De Almeida, C.M.S.; Ribeiro, A.S.; Saint'Pierre, T.D.; Miekeley, N. Studies on the origin and transformation of selenium and its chemical species along the process of petroleum refining. *Spectrochim. Acta Part B At. Spectrosc.* **2009**, *64*, 491–499. [CrossRef]
78. CEM Corporation. *Microwave Acid Digestion of Crude Oil Samples Using a New High Performance Vessel*; CEM Corporation: Matthews, NC, USA, 2017; Volume 4. Available online: https://cem.com/microwave-acid-digestion-of-crude-oil-samples-using-a-new-high-performance-vessel (accessed on 29 January 2026).
79. Duyck, C.; Jacobson, L.D.S.V.; De Souza, J.R.; Rocha, R.C.C.; Oliveira, C.J.; Da Fonseca, T.C.O.; Saint'Pierre, T.D. Brazilian basins characterization based on the distributions of elements in desalted crude oils using classical multivariate analysis and kohonen self-organizing map. *Geoenergy Sci. Eng.* **2023**, *223*, 211502. [CrossRef]
80. Heilmann, J.; Boulyga, S.F.; Heumann, K.G. Development of an isotope dilution laser ablation ICP-MS method for multi-element determination in crude and fuel oil samples. *J. Anal. At. Spectrom.* **2009**, *24*, 385–390. [CrossRef]
81. Henn, A.S.; Chernonozhkin, S.M.; Vanhaecke, F.; Flores, E.M. Development of methods for Mg, Sr and Pb isotopic analysis of crude oil by MC-ICP-MS: Addressing the challenges of sample decomposition. *J. Anal. At. Spectrom.* **2021**, *36*, 1478–1488. [CrossRef]
82. Trevelin, A.M.; Marotto, R.E.; De Castro, E.V.; Brandao, G.P.; Cassella, R.J.; Carneiro, M.T.W. Extraction induced by emulsion breaking for determination of Ba; Ca; Mg and Na in crude oil by inductively coupled plasma optical emission spectrometry. *Microchem. J.* **2016**, *124*, 338–343. [CrossRef]

83. Antes, F.G.; Dos Santos, M.d.F.P.; Lourenço Guimaraes, R.C.; Gottfried Paniz, J.N.; Moraes Flores, E.M.; Dressler, V.L. Heavy crude oil sample preparation by pyrohydrolysis for further chlorine determination. *Anal. Methods* **2011**, *3*, 288–293. [CrossRef]
84. Brenner, I.B.; Dorfman, E. Application of conventional and low-flow torches for the analysis of xylene-and tetralin-based petroliferous materials by argon and oxygen-argon ICP-AES. *Microchem. J.* **1995**, *52*, 81–95. [CrossRef]
85. Nadkarni, R.K.; Hwang, J.D.; Young, L. Multielement analysis of crude oils using inductively coupled plasma-atomic emission spectrometry. *J. ASTM Int.* **2011**, *8*, JAI103837. [CrossRef]
86. Brenner, I.B.; Zander, A.; Shkolnik, J. Determination of V, Ni and Fe in crude oils and bitumen using sequential ICP-OES and scandium as an internal standard. *Spectrometers* **2010**, *17*, 99–103. [CrossRef]
87. Silva, D.M.; Pereira, A.J.; Pierre, T.D.S.; Esteves, P.M.; Rocha, A.A.; Escalfoni, R., Jr.; Duyck, C. Automatized separation of fractions from petroleum based on spectrophotometric signal derivative using open-source hardware for the determination of Ni and V linked to porphyrins. *J. Braz. Chem. Soc.* **2019**, *30*, 1309–1317. [CrossRef]
88. Nelson, J.; Saunders, A.; Poirier, L.; Rogel, E.; Ovalles, C.; Rea, T.; Lopez-Linares, F. Detection of iron oxide nanoparticles in petroleum hydrocarbon media by single-particle inductively coupled plasma mass spectrometry (spICP-MS). *J. Nanoparticle Res.* **2020**, *22*, 304. [CrossRef]
89. Liu, J.J.; Selby, D. A matrix-matched reference material for validating petroleum Re-Os measurements. *Geostand. Geoanalytical Res.* **2018**, *42*, 97–113. [CrossRef]
90. Wang, M.; Chu, Z.; Meisel, T.C.; Guo, J. Determination of Re, Os, Ir, Ru, Pt, Pd Mass Fractions and $^{187}Os/^{188}Os$ Ratios of Organic-Rich Geological Reference Materials. *Geostand. Geoanalytical Res.* **2022**, *46*, 333–349. [CrossRef]
91. Sen, I.S.; Peucker-Ehrenbrink, B. Determination of Osmium Concentrations and 187Os/188Os of Crude Oils and Source Rocks by Coupling High-Pressure, High-Temperature Digestion with Sparging OsO4 into a Multicollector Inductively Coupled Plasma Mass Spectrometer. *Anal. Chem.* **2014**, *86*, 2982–2988. [CrossRef]
92. Chacon-Patino, M.L.; Nelson, J.; Rogel, E.; Hench, K.; Poirier, L.; Lopez-Linares, F.; Ovalles, C. Vanadium and nickel distributions in Pentane; In-between C5-C7 Asphaltenes; and heptane asphaltenes of heavy crude oils. *Fuel* **2021**, *292*, 120259. [CrossRef]
93. Kendall, B.; Wang, S.; Lillis, P.; Xing, L.; Zheng, W.; Zhu, C. Evaluation of the molybdenum isotope system as a petroleum tracer: The Phosphoria petroleum system; western USA. *Chem. Geol.* **2023**, *617*, 121244. [CrossRef]
94. Wang, S. Development of Molybdenum Isotopes as Petroleum Tracers: The Phosphoria Petroleum System, Bighorn Basin, USA. Doctoral Dissertation, University of Waterloo, Waterloo, ON, Canada, 2018. Available online: http://hdl.handle.net/10012/13333 (accessed on 22 May 2018).
95. Yang, W. A Method for High Precision Determination of Up to 57 Trace and Ultra-Trace Elements in Crude Oils Using Triple Quad-ICP-MS with Applications in Exploration, Production Allocation, and Refining. Doctoral Dissertation, University of Houston, Houston, TX, USA, 2019. Available online: https://hdl.handle.net/10657/5850 (accessed on 29 January 2026).
96. Gao, Y.; Casey, J.F.; Bernardo, L.M.; Yang, W.; Bissada, K.K. Vanadium isotope composition of crude oil: Effects of source; maturation and biodegradation. *Geol. Soc. Lond. Spec. Publ.* **2017**, *468*, 83–103. [CrossRef]
97. Udo, O.T.; Ekwere, S.; Abrakasa, S. Some trace metal in selected Niger Delta crude oils: Application in oil-oil correlation studies. *J. Min. Geol.* **1992**, *28*, 289–291.
98. Akinlua, A.; Ajayi, T.R.; Adeleke, B.B. Organic and inorganic geochemistry of northwestern Niger Delta oils. *Geochem. J.* **2007**, *41*, 271–281. [CrossRef]
99. Akinlua, A.; Adekola, S.A.; Swakamisa, O.; Fadipe, O.A.; Akinyemi, S.A. Trace element characterisation of Cretaceous Orange Basin hydrocarbon source rocks. *Appl. Geochem.* **2010**, *25*, 1587–1595. [CrossRef]
100. Jegede, T.O.; Adekola, S.A.; Akinlua, A. Trace element geochemistry of kerogens from the central Niger Delta. *J. Pet. Explor. Prod. Technol.* **2018**, *8*, 999–1007. [CrossRef]
101. Lewan, M.D.; Maynard, J.B. Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. *Geochim. Cosmochim. Acta* **1982**, *46*, 2547–2560. [CrossRef]
102. NaJi, M.; Corana, F.; Scilingo, A.; Scotti, R. Separation and characterization of vanadium and nickel organometallic compounds in heavy crudes. *Fuel Sci. Technol. Int.* **1994**, *12*, 593–611. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.