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Comparative evaluation of manual and microwave-assisted acid digestion methods for trace metal analysis in crude oil and its products using nitric and sulfuric acids

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Abstract

Accurate trace metal analysis in petroleum products is essential for refining efficiency, catalyst protection, and environmental compliance. This study compares manual acid digestion with microwave-assisted digestion (MAD) using the Anton Paar Multiwave 7000 for analyzing trace metals (V, Ni, Fe, Al, Mo) in crude oil total blend (251-20-17 O-3) and unconverted oil fractions (UCO, 390 °C cut). Manual digestion utilized nitric (HNO_3) and sulfuric (H_2SO_4) acids under atmospheric conditions, while MAD employed HNO_3 alone or a HNO_3-H_2SO_4 mixture in a nitrogen-filled pressurized digestion cavity (PDC). Inductively coupled plasma (ICP) analysis revealed MAD's superior performance in metal recovery and precision, with higher yields for V (2.56-6.26%), Fe (52.64-53.68%), and Al (3.84-14.95%) compared to manual digestion (V: 0.00%, Fe: 3.01-3.65%). Silicon (Si) recoveries were anomalously high (257.27-379.66%) in MAD due to contamination from borosilicate glass vials, rendering Si data unreliable. Nitrogen in the pressurized digestion cavity (PDC) suppressed boiling, prevented cross-contamination, and enabled higher digestion temperatures, reducing digestion time (115 min vs. 1-2 h) and enhancing safety. Manual digestion was labor-intensive and prone to analyte loss. These findings advocate for MAD with quartz or PTFE-TFM vials to avoid Si contamination, offering laboratories a faster, safer, and more accurate method for trace metal analysis in petroleum matrices.

Keywords: Acid digestion, microwave-assisted digestion (MAD), petroleum products, trace metals, Anton Paar Multiwave 7000

Introduction

Petroleum products, including UCO, are complex organic matrices containing trace metals from crude oil sources, refining processes, or additives. These metals, such as lead (Pb), nickel (Ni), vanadium (V), and copper (Cu), can impact fuel performance, catalyst poisoning, and environmental emissions (Speight, 2014) [10]. Accurate quantification requires complete mineralization of the organic matrix to release metals into a soluble form, typically achieved through acid digestion. Traditional manual acid digestion using nitric and sulfuric acids has been widely employed due to its simplicity and low equipment cost. Nitric acid acts as a strong oxidant to break down organic components, while sulfuric acid facilitates dehydration and removal of residual organics at elevated temperatures.

However, manual methods are labor-intensive, prone to incomplete digestion, and expose operators to hazardous fumes and acids. Microwave-assisted digestion (MAD) addresses these limitations by accelerating the reaction through dielectric heating in closed vessels, enabling higher temperatures and pressures for efficient mineralization. The Anton Paar Multiwave 7000, a semi-automated system with a pressurized digestion cavity (PDC), supports temperatures up to 300 °C and pressures up to 199 bar, accommodating various sample types including petroleum oils. This system uses pressure-sealed quartz or PTFE-TFM vials compatible with nitric and sulfuric acids, minimizing blank values and enabling low-volume digestions that is 2-4 mL (Kingston and Haswell, 1997) [4]. Previous studies have compared manual and microwave digestions for diverse matrices, showing MAD's advantages in speed and completeness for petroleum oils (Nadkarni, 2000) [8]. However, few focus on total blend and UCO using identical acid mixtures. This comparative study evaluates both methods for crude oil and its products digestion, assessing digestion efficiency, metal recovery, time, cost, and safety. The objective is to provide guidance for laboratories transitioning to automated systems.

Materials and Methods

Chemicals and Reagents

Concentrated nitric acid (HNO_3, 70% v/v) and sulfuric acid (H_2SO_4, 98% v/v) were obtained from Merck (Darmstadt, Germany). Deionized water was used for dilutions. Multi-element standard solutions metals such as Pb, Ni, V, and Cu were prepared from certified reference materials (CRM) from NIST (SRM 1643e).

Location and duration of study

The study was conducted in Lab 105, Analytical Department, Hydrocarbon Technology & Innovations LLC, New Jersey, USA, over a 72-hour period, including sample preparation and analysis.

Sample Preparation

251-20-17 O-3 total blend (crude oil) and UCO (390 °C cut) samples were prepared and 0.2g of each sample was accurately weighed into digestive vessels made from glass.

Manual Acid Digestion Procedure

Samples weighing 2.0 g were heated with 20 mL of H_2SO_4 at 100 °C for 30 minutes, then approximately 60 mL of HNO_3 was added, and digestion continued at 100-540 °C for 1-2 hours until the volume reduced to about 2.5-5.0 mL. The digest was then diluted with deionized water to 50 mL in a 50 mL volumetric flask. The digestions were performed in four replicates using Vycor beakers and subsequently analyzed via ICP in matrices of 10% H_2SO_4 and 10% HNO_3.

Semi-automated microwave-assisted digestion procedure

Using the Anton Paar Multiwave 7000 with a 24-position vial rack in a nitrogen-filled pressurized digestion cavity (PDC), 0.2 g samples of 251-20-17 O-3 total blend and UCO (390 °C cut) were digested in 10 mL borosilicate glass vials with 10 mL HNO_3 or in borosilicate glass vials with 8 mL HNO_3 and 2 mL H_2SO_4, capped with PTFE-TFM plugs, pre-digested at room temperature for 15 minutes and then at 100 °C in a water bath for 15 minutes, followed by a programmed temperature ramp (150 °C at 10 °C/min with 1000 W power at 50 bars, held for 30 min; 200 °C at 15 °C/min, held for 30 min; 250 °C at 15 °C/min, held for 30 min; cooled to 60 °C at 10 °C/min) over 115 minutes, with nitrogen suppressing boiling, preventing cross-contamination, and enabling higher temperatures for accurate analysis; digests were diluted to 50 mL in a 50mL volumetric flask and analyzed.

Data Analysis

The results were expressed as means ± SEM

Results

The data presented in Tables 1.0 to 5.0 illustrate significant variations in the trace element concentrations of the 251-20-17(15+16) total Blend and UCO 390 °C samples, influenced by the digestion method and acid treatment. Specifically, elements such as vanadium (V), nickel (Ni), iron (Fe), aluminum (Al), molybdenum (Mo), and silicon (Si) showed notable differences in concentrations between manual and semi-automated microwave-assisted digestion, with enhanced detection of certain elements in samples treated with HNO_3 or a combination of H_2SO_4 and HNO_3, indicating the impact of digestion conditions on elemental recovery.

Results

Table 1: The trace element concentrations of 251-20-17(15+16) total Blend for Manual Acid Digestion are presented as means ± SEM

	Trace elements (%)								
Sample	**V (292.401)**	**V (310.230)**	**Ni (232.003)**	**Ni (221.648)**	**Fe 259.940)**	**Fe (239.563)**	**Al**	**Mo**	**Si**
251-20-17(15+16) total Blend	0.00±0.00	0.00±0.00	3.65±0.05	3.50±0.07	3.01±0.04	3.15±0.03	-	0.70± 0.04	5.10±0.18

Table 2: The trace element concentrations of 251-20-17(15+16) total Blend for Semi-Automated Microwave-Assisted Digestion are presented as means ± SEM

	Trace elements (%)								
Sample	**V(292.401)**	**V(310.230)**	**Ni(232.003)**	**Ni(221.648)**	**Fe(259.940)**	**Fe(239.563)**	**Al**	**Mo**	**Si**
251-20-17(15+16) Blend + 10ml HNO_3	2.64±0.07	6.26±0.28	3.31±0.41	0.12±0.24	0.00±0.00	0.00±0.00	5.14±0.35	4.39±0.54	257.27±0.72

Table 3: The trace element concentrations of 251-20-17(15+16) UCO 390 °C for Manual Acid Digestion are presented as means ± SEM

	Trace elements (%)								
Sample	**V(292.401)**	**V(310.230)**	**Ni(232.003)**	**Ni(221.648)**	**Fe(259.940)**	**Fe(239.563)**	**Al**	**Mo**	**Si**
251-20-17(15+16) UCO 390°C	0.00±0.00	0.00±0.00	2.69±0.08	2.42±0.10	3.51±0.06	3.65±0.05	-	0.48±0.03	28.10±0.37

Table 4: The trace element concentrations of 251-20-17(15+16) UCO 390 °C for Semi-Automated Microwave-Assisted Digestion are presented as means ± SEM

	Trace elements (%)								
Sample	**V(292.401)**	**V(310.230)**	**Ni(232.003)**	**Ni(221.648)**	**Fe(259.940)**	**Fe(239.563)**	**Al**	**Mo**	**Si**
251-20-17(15+16) UCO 390°C + 10ml HNO_3	2.64±0.06	6.22±0.29	3.63±0.84	0.00±0.00	52.64±0.65	53.68±0.64	14.95±0.57	3.55±0.60	379.66±6.05

Table 5: The trace element concentrations of 251-20-17(15+16) total Blend for Semi-Automated Microwave-Assisted Digestion are presented as means ± SEM

	Trace elements (%)								
Sample	**V(292.401)**	**V(310.230)**	**Ni(232.003)**	**Ni(221.648)**	**Fe(259.940)**	**Fe(239.563)**	**Al**	**Mo**	**Si**
251-20-17(15+16) total Blend + 2ml H_2SO_4 + 8ml HNO_3	2.56±0.02	5.60±0.31	3.23±0.73	0.00±0.00	0.00±0.00	0.00±0.00	3.84±0.15	3.20±0.36	297.67±3.89

Discussion

This study compares the effectiveness of manual acid digestion and microwave-assisted digestion (MAD) using the Anton Paar Multiwave 7000 for trace metal analysis in crude oil (251-20-17 O-3 total blend) and unconverted oil fractions (UCO, 390 °C cut), with results summarized in Tables 1 to 5. Overall, MAD outperformed manual digestion in terms of efficiency, precision, and safety. The pressurized digestion cavity (PDC) in the MAD system provided a sealed environment that inhibited acid boiling, supported elevated digestion temperatures (up to 250 °C), reduced the risk of cross-contamination and volatile element loss, and shortened the process to just 115 minutes, in contrast to the 1-2 hours required for manual digestion (Anton Paar GmbH, 2018). Data from Tables 2, 4, and 5 indicate that MAD substantially improved recoveries for vanadium (2.56-6.26%), iron (52.64-53.68%), and aluminum (3.84-14.95%) relative to manual digestion, where vanadium was undetectable (0.00%), iron ranged from 3.01-3.65%, and aluminum was not detected (Tables 1 and 3). These improvements stem from the thorough mineralization of complex organic matrices achieved via precise dielectric heating in closed vessels (Flores *et al*., 2004; Bettinelli *et al*., 2000) [6, 2]. In comparison, manual digestion in open vessels, even at temperatures reaching 540 °C, was vulnerable to incomplete matrix decomposition and analyte volatilization (Murillo & Chirinos, 1994) [7]. That said, silicon recoveries in MAD (Tables 2, 4, and 5) were unusually elevated at 257.27-379.66%, attributable to leaching from borosilicate glass vials under acidic and high-temperature conditions, which compromised the reliability of silicon measurements (Korn *et al*., 2007) [5]. The combination of HNO_3 and H_2SO_4 in MAD (Table 5) yielded modest gains in vanadium and aluminum recoveries but failed to mitigate silicon contamination. Nickel levels in MAD samples (Tables 2, 4, and 5) varied widely (0.00-3.63%), possibly owing to matrix effects or partial dissolution, whereas manual digestion (Tables 1.0 and 3.0) yielded more uniform nickel concentrations (2.42-3.65%) (Bettinelli *et al*., 2000) [2]. Refining MAD protocols or incorporating ICP-MS could enhance nickel detection accuracy. In general, MAD exhibited greater precision for vanadium, iron, and aluminum (Tables 2, 4, and 5) than manual digestion (Tables 1 and 3), though exceptions occurred for nickel and molybdenum, where manual results were influenced by procedural inconsistencies and potential contamination. Safety was notably improved with MAD, thanks to its enclosed design featuring overpressure vents, which limited exposure to acid vapors in ways that fume hoods alone could not achieve during manual procedures. Although manual digestion remains a budget-friendly option for resource-limited settings, the upfront investment in MAD is justified by its lower labor demands, higher sample throughput (up to 24 samples at once), and reduced reagent volumes (2-10 mL versus 20-60 mL), (Sneddon *et al*., 2006) [9]. Key limitations encompass the observed silicon contamination and the lack of validation against certified reference materials. Moving forward, research should prioritize quartz or PTFE-TFM vials for reliable silicon analysis and explore varied acid combinations to confirm MAD's robustness, ultimately promoting its use in high-volume petroleum testing.

Conclusion

The Anton Paar Multiwave 7000, leveraging nitrogen-assisted PDC, offers significant advantages over manual digestion for trace metal analysis in petroleum products, providing higher recoveries, better precision, faster digestion, and enhanced safety. However, the use of appropriate vial materials is critical to avoid Si contamination. These findings support the adoption of MAD in analytical laboratories, particularly for high-throughput analysis of complex petroleum matrices, with implications for refining optimization and environmental compliance.

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