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An approach to determining nickel, vanadium and other metal concentrations in crude oil

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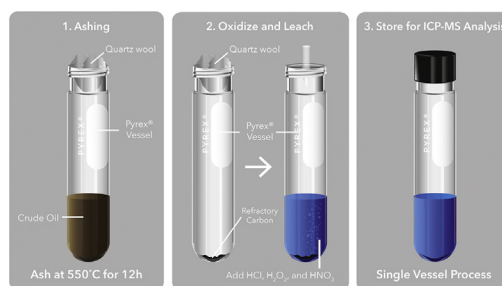
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HIGHLIGHTS

- Single vessel ashing-digestion-ICPMS provides an accurate method for determining metal concentrations in crude oil.
- This method successfully addresses criticisms about the reliability of crude oil analyses that involve ashing.
- The method is applicable both to light crude oils and heavy crude oils with a large asphaltene fraction.

GRAPHICAL ABSTRACT



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ABSTRACT

The ability to accurately determine the metal content of crude oils is necessary for reasons ranging from the need to identify the source of the oils (Ni and V) to removing components that might inhibit catalysis during refining or impact negatively on the environment during hydrocarbon combustion. Here we show that ashing followed by chemical oxidation and acid digestion, coupled with ICP-MS analysis, provides an accurate method for determining the concentration of metals in crude oil. Nickel and vanadium concentrations were measured in certified Ni and V oil standards and in various light, intermediate and heavy crude oils after application of a single vessel ashing-chemical oxidation-acid digestion sample preparation and storing technique. Prior to the ashing, chemical oxidation and acid digestion, an aliquot of the crude oil was placed in a 10 ml Pyrex™ culture tube and capped with quartz wool. The capped culture tubes were then subjected to thermal combustion, followed by chemical oxidation and leaching. The leachates and the aqueous standards were diluted and analyzed for their Ni and V contents using inductively coupled plasma mass spectrometry (ICP-MS).

The measured concentrations of Ni in oil standards, reported to contain 1, 100, and 1000 mg kg⁻¹ Ni ($\pm 2\%$ error), were 1.1 ± 0.01 , 99.8 ± 1.46 , and 1025 ± 24 mg kg⁻¹ respectively. The corresponding concentrations of V in these standards, reported to contain 2, 100, and 1000 mg kg⁻¹ V, were measured to be 1.93 ± 0.06 , 104 ± 1.3 , and 1027 ± 7.5 mg kg⁻¹, respectively. Crude oil samples, A, B, C, D and E, that varied significantly in their composition, and ranged from light to heavy, were determined to contain 5.59 ± 0.32 , 4.05 ± 0.03 , 6.22 ± 0.22 , 33.8 ± 0.7 and 41.6 ± 3.5 mg kg⁻¹ Ni, respectively. Their V contents were determined to be 11.98 ± 0.1 , 12.2 ± 0.1 , 16.5 ± 0.4 , 34.7 ± 0.4 , and 104 ± 8.9 mg kg⁻¹, respectively. The results were thus repeatable on average to 4.1% and 2.75% for Ni and V, respectively; the repeatability was worst ($\sim 8.5\%$) for crude oil E, a heavy (viscous) oil with a very high asphaltene content (27.2%).

This modified single vessel ashing-digestion technique (combustion, chemical oxidation, acid leaching and storing) minimizes contamination and significantly reduces the loss of ash. Our results are repeatable, comparable to, and in some cases superior to those of other methods. The method is applicable to a

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wide range of crude oil compositions, is very accessible and robust, easy to use, and does not require costly equipment in preparing the samples for analysis by ICP-MS.

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1. Introduction

Accurate determination of metal concentrations in crude oils to low levels of detection is needed for a variety of reasons. For example, some metals (e.g., Ni, Co, Pd, Pt, and S) may poison catalysts used in refining oils, thereby reducing their effectiveness, some metals (e.g., Cr, Fe, Al, and Cu) may cause corrosion in oil-fired power plants, whereas other metals (e.g., Pb, Hg, Cr, Ni, Cd, and As), will impact negatively on the environment, if released to the atmosphere (even in low concentrations) during the combustion of petroleum products [1–9]. The two metals that consistently have the highest concentrations in crude oils are Ni and V (up to 1000 mg kg⁻¹ and 200 mg kg⁻¹, respectively) [9–12], although their absolute concentrations vary considerably among different crude oils. Because of their high and variable concentrations, these two metals are analyzed routinely in crude oil to identify the source regions and determine the migration paths of the hydrocarbons [1,2,13,14]. Analysis for these metals has also proven helpful in evaluating crude oil maturation, because mature oils have lower concentrations of Ni and V porphyrins than immature oils, and to assign responsibility in the case of oil spills [2,6,15,16]. The current investigation, however, was motivated by a need to be able to analyze crude oils that had been reacted with metals as part of a project designed to test the hypothesis that liquid hydrocarbons might constitute ore fluids for some deposit types.

Metal concentrations in crude oil can be determined either by direct instrumental analysis with little or no sample preparation (refer to Table A.1 in Appendix A in the supplementary material), or with a destructive method of sample preparation that decomposes the oil and is followed by instrumental analysis (refer to Table A.2 in Appendix A in the supplementary material). The former determinations are made with neutron activation analysis (NAA), graphite furnace atomic absorption spectrometry (GF-AAS), inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). Only NAA, however, requires no sample preparation. The other three techniques require the crude oils to be diluted (e.g., with xylene or toluene) or emulsified prior to instrumental analysis (refer to Table A.1. in Appendix A in the supplementary material). These techniques are much less time-consuming than the destructive techniques, which generally involve relatively complex sample preparation procedures e.g. [17,18]. However, the detection limits are higher and the accuracy lower. The lower accuracy is because these techniques require the use of aqueous or oil standards, which have a matrix that is different from the complex matrix of the crude oil sample [19–22]. For further discussion of the problems associated with direct analysis of crude oils, readers are referred to the reviews of Filby and Olsen (1994) and Mello et al. (2012).

Destructive sample preparation consists either of chemical oxidation/acid digestion (oxidation and leaching of crude oil with acids, e.g., HNO₃ + HCl) or a combination of ashing and acid digestion (thermal combustion followed by acid digestion; refer to Table A.2. in Appendix A in the supplementary material). The former preparation typically makes use of a high-pressure asher (HPA; acid digestion using a quartz reactor) e.g. [22,24], a

microwave oven (microwave-induced acid digestion, MIC; acid digestion using a polytetrafluoroethylene (PTFE™) - TFM™ lined reactor) e.g., [8, 22,24,25], or simply a beaker and a hotplate (ASTM D5708-15) e.g. [23]. In all three methods, an aliquot of oil is added to a large volume of acid either in a closed (HPA or MIC) or an open vessel (ASTM D5708-15) to destroy the organic matrix and dissolve the associated metals. Although, HPA and MIC yield highly repeatable and reproducible results, the equipment is costly and can be inaccessible, and the number of samples that can be digested per session is relatively small (approximately four quartz vessels for HPA and 12 PTFE™-TFM™ lined vessels for MIC per session; there are more expensive systems that can digest organic materials in up to 168 samples, e.g., NovaWave but these are not commonly used in research laboratories). Furthermore, although the vessels for MIC and HPA contain safety mechanisms to prevent over-pressurization, if the safety membrane (MIC) or cap (HPA) opens, the acids can spill out of the vessels, thereby creating a risk to safety. The ASTM D5708-15 method, in contrast, is very simple to use, safe and inexpensive. However, as it utilizes an open beaker, there is a high probability of contamination and loss of acid, leading to poor reproducibility of results.

Combined dry-ashing and acid digestion involves placing an aliquot of the crude oil sample in a platinum (Pt) or quartz crucible and heating it to ~ 450 to 550 °C under a 1 bar oxygen atmosphere [26]. This removes most of the organic matrix [26–28]. Nitric acid or sulfuric acid is then added to the crucible, which serves to oxidize the remaining ash and leach the metals. The digested samples are then diluted for further analysis (e.g., AAS, ICP-MS, and ICP-OES). Although this method is simple, safe, and affordable, it has been strongly criticized because of poor metal recovery due to volatilization and loss of ash, the large volume of sample required (up to 20 ml) and the long preparation time e.g. [20–22,24,26].

Below, we describe a modification of the combined ashing and chemical oxidation/acid digestion method of preparation, which addresses the above criticisms. In this method, 5 g crude oil samples are ashed, chemically oxidized, and leached in narrow disposable Pyrex™ culture tubes capped with quartz wool to prevent material loss (e.g., volatile elements, volatile compounds, or oil) during combustion. This modification reduces the sample size considerably, allows ashing, chemical oxidation, leaching and storage to be done in the same reactor, thereby minimizing the risk of contamination, and greatly increasing the number of samples that can be ashed simultaneously. Most importantly, the modification yields highly reproducible metal concentrations with an accuracy comparable, and in some cases superior, to those that have been reported for other methods.

2. Material and methods

2.1. Sample description

Nickel and vanadium crude oil standards were purchased from the Conostan® division of SCP Science Ltd (refer to Appendix G for more information). The selected certified oil standards had been analyzed according to the protocol proposed by the American Society of Testing Material (ASTM) D5708 (classic wet chemistry method) using the appropriate NIST standards. The nickel oil

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