

FEASIBILITY OF MICROWAVE-ASSISTED SINGLE REACTION CHAMBER FOR DIGESTING CRUDE OIL AND ITS FRACTIONS

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Introduction

Crude oil and its fractions (atmospheric residue-AR and vacuum residue-VR) are hydrocarbon-based matrices, containing also some elements, such as sulfur, nitrogen, oxygen and metals. These contaminants are naturally present or can be introduced in crude oil during its production, transport and storage¹. Even in trace amounts, they can result in corrosion, catalyst poisoning and can impair the quality of refined products, in addition to contribute to environmental pollution. Thus, the determination of contaminants is an important task for technological and environmental purposes. However, for crude oil and its fractions it is difficult to apply conventional procedures for sample preparation due to matrix complexity. In this work, digestion of crude oil and its fractions is proposed by using microwave-assisted single reaction chamber² for further metals and sulfur determination by inductively coupled plasma optical emission spectrometry (ICP OES).

Results and Discussions

Samples were digested using an ultra high pressure microwave-assisted digestion system (single reaction chamber, MAWD-SRC, UltraWave™, Milestone, Italy) equipped with five quartz vessels (40 mL). Comparatively, microwave-assisted wet digestion in closed vessels (MAWD) was performed using a microwave oven (Multiwave 3000®, Anton Paar, Austria) with eight quartz vessels (80 mL). The determination of Al, Ba, Ca, Co, Cr, Fe, Mg, Ni, V, and S, as well as residual carbon content (RCC), was performed by ICP OES using an axial view spectrometer (Optima 4300 DV, Perkin Elmer, Shelton, USA), equipped with a cyclonic spray chamber and a concentric nebulizer. Instrumental parameters for the determination were set according to the manufacturer recommendations. Sample masses from 100 up to 1000 mg were evaluated for both systems, as well as the concentration of HNO₃ (10 and 14 mol L⁻¹) and its mixture with H₂O₂ (50%). The conditions used in both methods are shown in Table 1.

Table 1: Experimental conditions used in MAWD and MAWD-SRC methods.

Method	Time (Ramp, min)	Time (Hold, min)	Power (W)	T (°C)	P (bar)
MAWD	10	10	400	205*	80
	10	10	1400	205*	80
	20		0		
MAWD-SRC	10	10	-	80	160
	10	10	-	250	160
	40		0		

* Correspondent to the maximum temperature obtained during digestion procedure.

Contrarily to MAWD, where it was possible to digest 500 mg, the proposed MAWD-SRC method allowed the digestion of up to 750 mg of sample. In these conditions, RCC was about 24 and 17%, respectively, for heavy crude oil and its fractions (AR and VR). Accuracy was evaluated by using certified reference materials (NIST 1634c, residual fuel oil) for Ba, Co, Ni, V and S, and results were in agreement with certified values ($P < 0.05$) for all analytes. Limits of detection from 0.014 (for Mn) up to 4.8 $\mu\text{g g}^{-1}$ (for S) were obtained using MAWD-SRC, which were better than those obtained using MAWD.

Conclusions

The proposed method was suitable for metals and sulfur determination in heavy crude oil and its fractions showing advantages due to the possibility to digest larger sample masses (750 mg) allowing low detection limits. Furthermore, the proposed system presented higher digestion efficiency allowing accurate determination of elements by ICP OES.

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¹J.G. Speight, John Wiley and Sons Inc, New Jersey, 2001, 519 pp.

²Nóbrega, J.A. et al. *Talanta* 2012, 98, 272-276.