

Electronic Supplementary Information (ESI)

Development of Methods for Mg, Sr and Pb Isotopic Analysis of Crude Oil by MC-ICP-MS: Addressing the Challenges of Sample Decomposition

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Table S1. Instrument settings and data acquisition parameters for the Thermo Scientific Neptune MC-ICP-MS instrument.

Instrument settings							
	Mg		Sr		Pb		
RF power, W			1200				
Cool gas, L min ⁻¹			15				
Auxiliary gas, L min ⁻¹			0.6-0.8 ^a				
Nebulizer gas, L min ⁻¹			0.9-1.1 ^a				
Sampling cone			Ni, Jet-type: 1.1 mm orifice diameter				
Skimmer cone			Ni, X-type: 0.8 mm orifice diameter				
Sample uptake, mL min ⁻¹			0.1				
Mass resolution mode	Medium ^b		Low				Low
Data acquisition parameters							
Mode	Static, multi-collection						
Integration time, s			4.194				
Number of integrations/blocks/cycles	3/10/5		1/6/5				1/7/6
Approach for instrumental mass discrimination correction	SSB		Russell's law using ⁸⁸ Sr/ ⁸⁶ Sr = 8.375209 + SSB				Baxter's correction using Tl + SSB
Cup configurations							
Mg cup configuration	L3: ²⁴ Mg	C: ²⁵ Mg	H3: ²⁶ Mg				
Amplifier, Ω	10 ¹¹	10 ¹¹	10 ¹¹				
Sr cup configuration	L4: ⁸² Kr	L3: ⁸³ Kr	L2: ⁸⁴ Sr	L1: ⁸⁵ Rb	C: ⁸⁶ Sr	H1: ⁸⁷ Sr	H2: ⁸⁸ Sr
Amplifier, Ω	10 ¹¹	10 ¹¹	10 ¹¹	10 ¹¹	10 ¹¹	10 ¹¹	10 ¹¹
Pb cup configuration	L3: ²⁰² Hg	L2: ²⁰³ Tl	L1: ²⁰⁴ Pb	C: ²⁰⁵ Tl	H1: ²⁰⁶ Pb	H2: ²⁰⁷ Pb	H3: ²⁰⁸ Pb
Amplifier, Ω	10 ¹³	10 ¹¹	10 ¹³	10 ¹¹	10 ¹¹	10 ¹¹	10 ¹¹

^a Optimised daily for maximum analyte intensity.

^b Δm for pseudo-high resolution in MC-ICP-MS is defined as the difference between masses corresponding to 5 and 95 % of the signal intensity at the plateau. A resolving power of 3800 was measured for the medium mass resolution mode. Such a definition exceeds that based on atomic mass difference (10% valley definition) roughly two-fold.¹

Table S2. Summary of sample preparation methods reported in the literature for Sr and Pb isotopic analysis of crude oil.

Analyte	Sample preparation and analyte isolation procedure	Technique	Ref.
Sr	3.5 g of crude oil were digested with a mixture of HNO ₃ and H ₂ O ₂ at 120 to 160 °C. Then, samples were ashed in a muffle furnace at 300 to 350°C for 8 h. Residues were dissolved in 2 mol L ⁻¹ HNO ₃ and Sr isolation was performed using Sr-Spec resin. After matrix elution with 7 mol L ⁻¹ HNO ₃ , the Sr fraction was eluted using 0.05 mol L ⁻¹ HNO ₃ .	TIMS	2
Pb	5 ml of crude oil were dissolved in dichloromethane and mixed with 1.5 mol L ⁻¹ HBr. After mixing, the aqueous phase (HBr) was separated and collected. After collection, HBr was added again to the organic phase and the extraction repeated. Aqueous phases were evaporated to dryness overnight (110 °C) and residues were digested using a mixture of HNO ₃ and H ₂ O ₂ . Finally, 6 mol L ⁻¹ HCl was added and the samples were evaporated to dryness. Residues were dissolved in 2 mol L ⁻¹ HBr and Pb isolation was performed using AG1-X8 resin. After matrix elution with 2 mol L ⁻¹ HBr, the Pb fraction was eluted using 6 mol L ⁻¹ HCl.	MC-ICP-MS	3, 4
Pb	0.5 g of crude oil were digested in a high-pressure asher with a mixture of HNO ₃ and H ₂ O ₂ at 320 °C for 90 min. For some samples it was necessary to digest 4 aliquots of 0.5 g due to the low Pb concentration. The four digests were combined and evaporated to dryness. The residue was dissolved in 2% HNO ₃ . For derivatization, samples were mixed with a buffer solution and the pH was adjusted to 4.9. Then, isooctane and 1% NaBEt ₄ were added and the mixture was manually shaken for 5 min. The isooctane supernatant was collected for analysis.	GC-MC-ICP-MS	5
Pb	Sample preparation was performed as described above for reference 17. After evaporation of the digests, the residues were dissolved in 0.5 mol L ⁻¹ HBr and centrifuged for 20 min at 4000 rpm. Pb isolation was performed using AG1-X8 resin. After matrix elution with 0.5 mol L ⁻¹ HBr and 0.2 mol L ⁻¹ HCl, the Pb fraction was eluted using 6 mol L ⁻¹ HCl.	MC-ICP-MS	6
Mg, Sr and Pb	<i>i</i>) 0.5 g of crude oil were digested by MAWD-PDC using 14.4 mol L ⁻¹ HNO ₃ at 250 °C for 75 min. <i>ii</i>) 2 to 10 g of crude oil were solubilized in toluene (at 90 °C) and filtered through a nylon membrane filter. The membrane was washed with hot toluene (at 90 °C), dried in an oven (105 °C) and transferred into a vessel containing ultrapure water for analyte dissolution. After evaporation at 90°C (for both, MAWD-PDC and ASTM procedures) the residues were dissolved as follows: in 0.4 mol L ⁻¹ HCl for Mg isolation or in 7 mol L ⁻¹ HNO ₃ for Sr and Pb isolation. Mg isolation was performed using AG50WX8 strong cation exchange resin. After matrix elution with 0.4 mol L ⁻¹ HCl and 0.5 mol L ⁻¹ HCl: 95% acetone (only for digests), the Mg fraction was eluted using 0.8 mol L ⁻¹ HCl. Sr and Pb isolation were performed using a Sr-spec resin. After matrix elution with 7 mol L ⁻¹ HNO ₃ , the Sr and Pb fractions were eluted with H ₂ O and 8 mol L ⁻¹ HCl, respectively.	MC-ICP-MS	This work

Table S3. Elemental composition of crude oil D obtained upon MAWD-PDC or solubilization. Results obtained via SF-ICP-MS (mean \pm standard deviation, n = 3).

Element	Concentration, $\mu\text{g g}^{-1}$	
	MAWD-PDC	Solubilization
Al	9.96 \pm 0.70	-
Be	< 0.005 ^a	< 0.005 ^a
Ca	512 \pm 36	506 \pm 20
Fe	29.8 \pm 1.8	-
K	56.7 \pm 4.0	50.9 \pm 3.7
Mg	199 \pm 10	201 \pm 9
Mn	3.09 \pm 0.22	-
Na	2930 \pm 268	2824 \pm 130
Pb	0.193 \pm 0.017	-
Rb	0.144 \pm 0.010	0.117 \pm 0.007
Sr	20.3 \pm 1.0	19.5 \pm 1.1
Ti	< 0.05 ^a	< 0.05 ^a
Zn	1.20 \pm 0.10	-

^a LOQ (10 SD) obtained by SF-ICP-MS

Reference

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