Ultra trace Hg determination in crude oils by CV-ICP-MS: overcoming the limitations of sample preparation to determine sub-ppb levels

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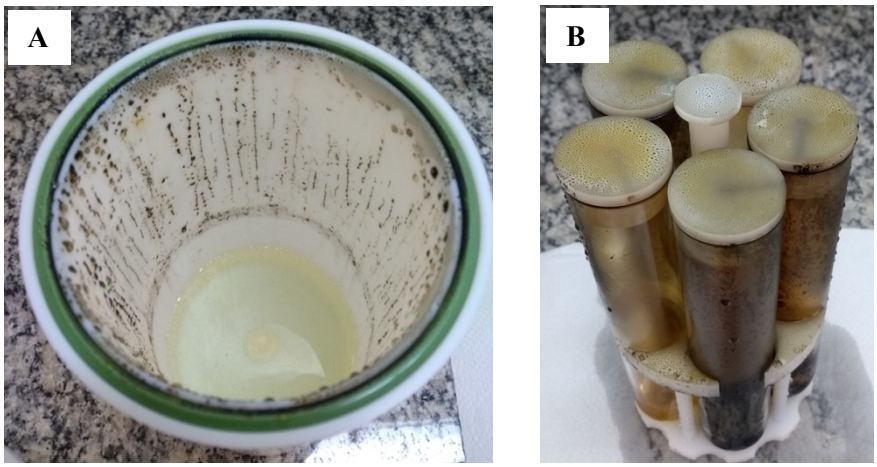

Figure S1. Aspects of the (A) PTFE vessel (cavity) and (B) digestion vessels, after crude oil digestion by MAWD-PDC using the recommended microwave irradiation program. Conditions: 0.5 g of Crude oil 1, 6 mL of 14.4 mol L^{-1} HNO_3 270 ºC and 20 min at 270 ºC.

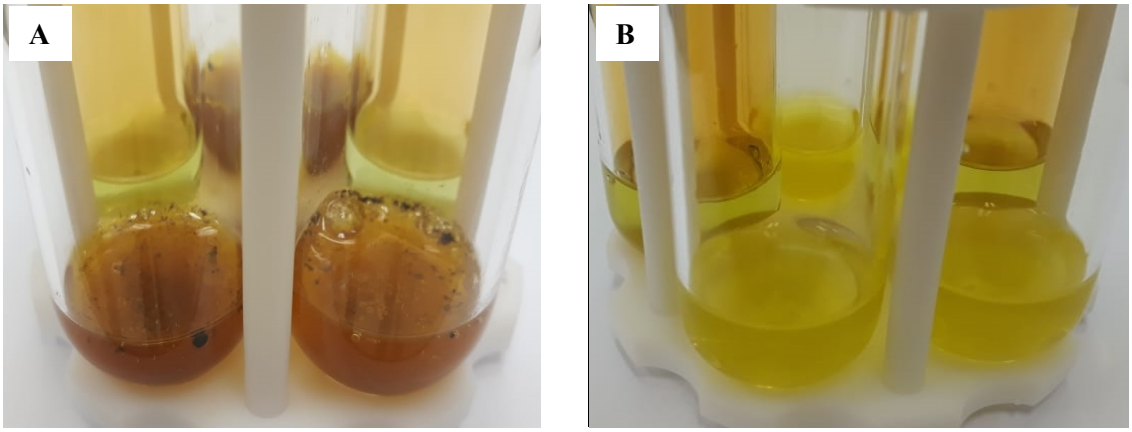

Figure S2. Aspects of the digests of Crude oil 1 after digestion by MAWD-PDC using 1.2 g with (A) 6 mL and (B) 8 mL of HNO_3. Conditions: *i*) 5 min of ramp to 90 ºC; *ii*) 10 min up to 110 °C; *iii*) 10 min up to 120 °C; *iv*) 10 min up to 130 °C; *v*) 15 min up to 140 °C; *vi*) 15 min up to 270 °C (hold for 20 min).

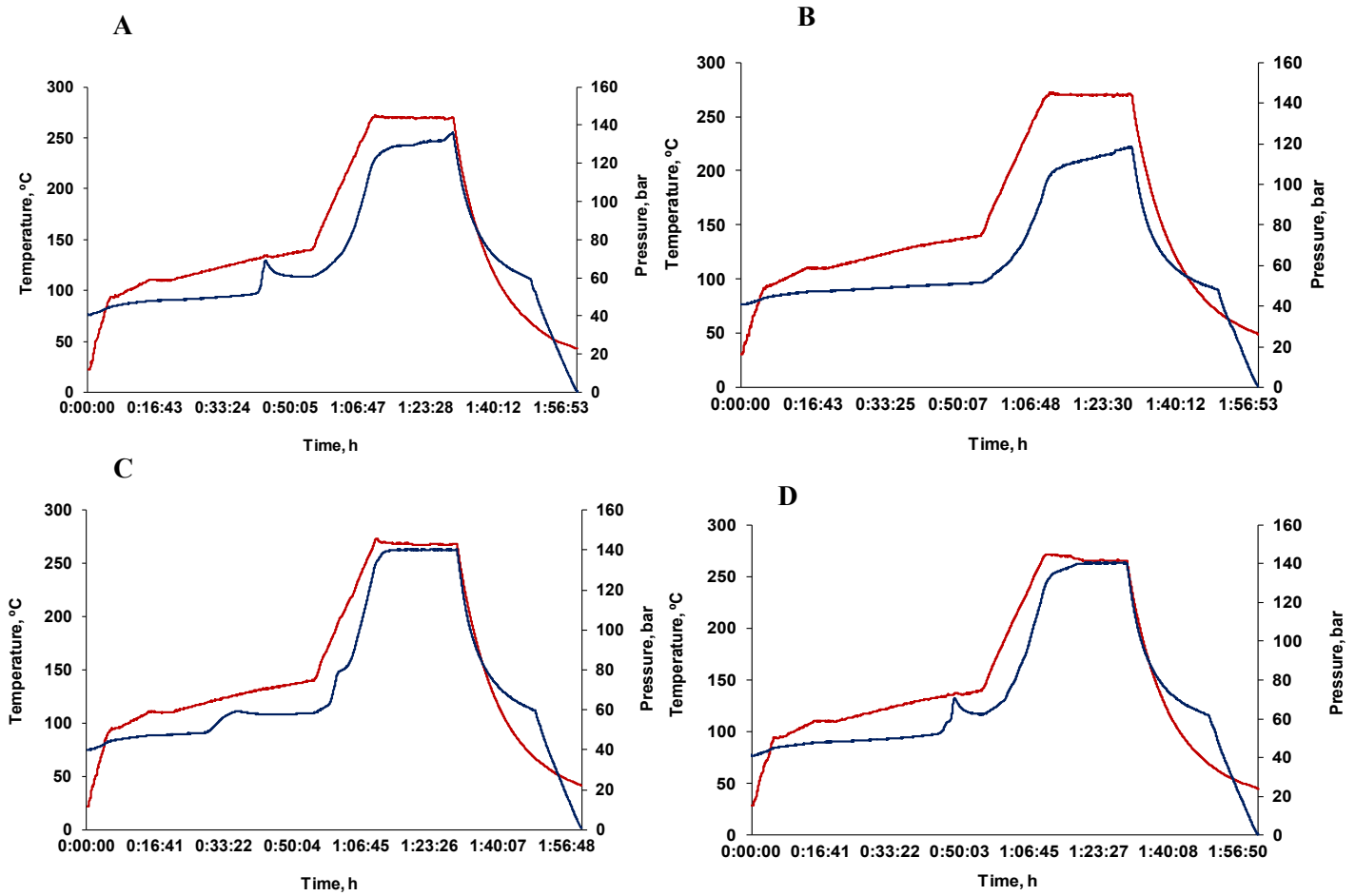

Figure S3. Irradiation program profiles for (A) Crude oil 1 (medium), (B) Crude oil 3 (heavy), (C) Crude oil 4 (heavy) and (D) Crude oil 6 (light). The red line corresponds to temperature profile and the blue line corresponds to pressure profile. Conditions: 1.2 g of crude oil, 8 mL of HNO_3, and *i*) 5 min of ramp to 90 ºC; *ii*) 10 min up to 110 °C; *iii*) 10 min up to 120 °C; *iv*) 10 min up to 130 °C; *v*) 15 min up to 140 °C; *vi*) 15 min up to 220, 250 or 270 °C (hold for 20 min) 270 °C.

Table S1. Other reported methods for sample preparation of crude oil for Hg determination and respective LODs.

Sample preparation	General conditions	Analytical technique	LOD
Thermal decomposition[1]	0.3 g of alumina and about 25 mg of sample. Air flow rate of 0.7 L min^{-1} was used to release Hg formed in the reduction reaction. Air flow rate of 0.8-1.2 L min^{-1} and temperatures of 350-450 °C 600-770 °C and 680-730 °C were used for the sample decomposition in the first (evaporator) and second (after burner) chambers and analytical cell of the PYRO-915+ pyrolyzer, respectively.		11.0 ng g^{-1}*
Combustion[5]	0.1 g of sample. The temperature of the chamber for atomization is around 700-750ºC.	CV-AAS with Zeeman background correction	n.i
Combustion-gold amalgamation[6]	0.1 g of sample. Amalgamator temperature at 600 ºC. Catalytic section of furnace at 850 ºC.	CV-AAS	n.i
Direct analysis[13]	30 µL of emulsions of sample. Pyrolysis temperature at 400 ºC. Atomization temperature at 1400 ºC.	ETAAS	0.78 µg L^{-1}*
Direct analysis[16]	2 mL of emulsion of sample (50% v/v), propan-1-ol (48% v/v) and water (2% v/v).	PVG-AAS	0.6 µg L^{-1}
Extraction[14]	5 g of sample and 10 µL of a mixture of BrCl/HCl (oxidizing solution). Agitation for 30 min. Centrifugation for 15 min.	CV-AFS	0.38 µg kg^{-1}
Extraction[15]	20 mL of sample and 4 mL of extraction solution (2.5% m/v triton X-100 and 15% v/v HNO_3). Agitation for 30 min at 80 ºC.	CV-AAS	1.9 µg L^{-1}
MAWD-PDC – the proposed method	**1.2 g of sample, 8 mL of concentrated HNO_3, and 85 min of the heating program (plus 20 min for cooling).**	**CV-ICP-MS**	**0.16 ng g^{-1} or (7.2 ng L^{-1})**

*Limit of quantification
n.i: Not informed
CV-AAS: cold vapor atomic absorption spectrometry;

CV-AFS: cold vapor atomic fluorescence spectrometry;
ETAAS: electrothermal atomic absorption spectrometry;
ID-CV-ICP-MS: isotope dilution cold-vapor inductively coupled plasma mass spectrometry;
PVG-AAS: photochemical vapor generation atomic absorption spectrometry.