

# ARSENIC QUANTIFICATION IN HEAVY DISTILLATES BY ICP-MS

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Arsenic content in petroleum distillates is important because, even at very low amounts, it can influence the activity performance of hydroprocessing catalysts [1]. Moreover, As content is assessed to estimate possible environmental impacts (emission and site contamination).

Table 1  
Arsenic in Crude Oils

Oil Type	Total Arsenic (ppm)
Alaska	24
Alaska	24 to 111
California	83 to 1932
Utah	77 - 243
Louisiana	~ 45
Venezuela	20-254
Wyoming	111

Distillation Cut	Percent of Total	Distillation Cut	ppm
Total	20 ppm (Venezuela)		4.6 ppm (Brow Oil)
Distillate	15	Light Oil	<DL
LVO	4	Light Distillate	1.4
HVO	25	Heavy Distillate	4.4
Residuum	56	Residuum	2

Arsenic content ranges from ppb to ppm, depending on the crude oil origin (Table 1) [1]. The behavior is different from other elements and As is distributed throughout the whole boiling range even if, generally, it can be found more enriched in the heavy distillation cuts.

A large number of papers is available for the quantification of arsenic in petroleum distillates [2], [3], [4], [5], [6] generally carried out with GF-AAS. ICP-MS is less used, because of the only available isotope <sup>75</sup>As and the mass interferences such as <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup> and <sup>40</sup>Ca<sup>35</sup>Cl<sup>+</sup> (false positives).



Aim of the work was the quantification of arsenic by ICP-MS, after MW digestion. The collision cell mode (H<sub>2</sub> and He gas) was used to check for possible interferences.

Sample preparation: MW digestion (Milestone ETHOS MOD) was performed using TFM vessels and quartz inserts. Only 3 cc HNO<sub>3</sub> and 1 cc H<sub>2</sub>O<sub>2</sub> were required for 0.150- 0.300 g sample. A slow increasing temperature digestion programme (25' up to 205°C) was needed. At the end, if necessary, samples solutions (from lower masses) can be concentrated at 150°C.



Fig 1: 400-500°C distillation cut sample



Preliminary trials on the new apparatus "ULTRAWAVE" MILESTONE showed better simplicity, efficacy and efficiency of the digestion



Fig 2: AGILENT 7500ce ICPMS

Instrumental quantification by ICP-MS. He and H<sub>2</sub> collision cell (flow 3.7 ml/min) were used. External instrumental calibration was performed by means of 2% v/v HNO<sub>3</sub> aqueous standard solutions. <sup>89</sup>Y was the internal standard.

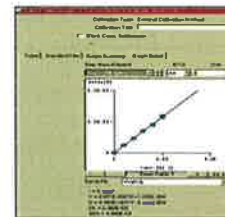


Fig 3: example of calibration (H<sub>2</sub> gas in the collision cell) Instrumental DL: 2-3 ng/l

Table 2: results for 10 replicates

sample	As	sd	CV
	mg/kg		%
1223	0.28 <sub>2</sub>	0.026	9.2
1231	0.06 <sub>8</sub>	0.0028	4.1

Short and intermediate precision



Table 2 shows the average values for the three instrumental conditions. No interference was detected on this kind of samples.



- ✓ very low quantities of acid are needed in comparison of UOP method [6]
- ✓ faster procedure
- ✓ comparable precision
- ✓ method LOQ is 15 ppb, better than UOP's
- ✓ ICP-MS instrumental elemental quantification could be easily applied to other analytes



[1] ART advanced refining technologies publication (Issue 108/2010)  
 [2] E. Beker, R.T. Rampazzo, M.B. Dessuy et Al, Spectrochimica Acta Part B, 66 (2011) 345.  
 [3] J. G. Pedrini Brandao, R. Calixto de Campos et Al, Spectrochimica Acta Part B, 63 (2008) 880  
 [4] J. Meira Trindade, A. Lopes Marquez et Al, Fuel 85 (2006) 2155-2161.  
 [5] M. Tarunen, S. Peraniemi, Analytica Chimica Acta 311 (1995) 85-91  
 [6] UOP 986-08 "Arsenic in heavy petroleum fractions using microwave digestion and GF-AAS"



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