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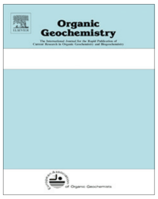

Multi-element analysis of crude oils using ICP-QQQ-MS

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A B S T R A C T

Determination of trace element contents in crude oils constitutes a powerful geochemical tool, complementing organic geochemical analyses and allowing a deeper insight into the processes of oil generation, migration and maturation. Inductively coupled plasma mass spectrometry (ICP-MS) has been widely applied to trace element determination in petroleum samples due to its low detection limits and fast multi-element capability. However, quantification of several elements by quadrupole-based ICP-MS is hampered by low sensitivity due to high ionisation energy, severe polyatomic interferences and/or low abundance. In the present contribution an ICP tandem mass spectrometer (ICP-MS/MS), or triple quadrupole ICP-MS (ICP-QQQ-MS) has been used to overcome these limitations. Prior to analysis, samples were subjected to high pressure acid digestion, allowing external calibration by means of aqueous standards. 25 elements, including P, S, the first-row transition metals, As, Se, Re, Pb and U, could be quantified in one measurement. Polyatomic interferences on the lighter elements could be removed by reaction of the target ions with O_2 or NH_3 in the collision/reaction cell of the ICP-MS/MS. The accuracy of the analytical method was assessed by the analysis of the standard reference materials NIST SRM 1634c (trace elements in fuel oil) and 1084a (wear-metals in lubricating oil). The measurement procedure was applied to the analysis of crude oil samples from the Alpine Foreland Basin of Austria.

1. Introduction

Data on trace element contents in crude oils and related products are considered useful in several respects (Sánchez et al., 2013): Aside from refining and environmental considerations (Ali and Abbas, 2006), the concentration and distribution of trace elements can provide valuable information on origin, migration, depositional environment and maturation of oils (Lewan and Maynard, 1982; Lewan, 1984; Barwise, 1990; Filby, 1994). In addition, acquiring Re data can help to identify samples for the application of the Re-Os isotope system for age determination (Selby and Creaser, 2005; Selby et al., 2007).

Inductively coupled plasma techniques (ICP-OES and ICP-MS) have been widely applied to trace element determination in petroleum related samples (Sánchez et al., 2013), including crude oils (Hardaway et al., 2004; Duyck et al., 2007), automotive fuels (Korn et al., 2007) and lubricating oils (Aucélio et al., 2007), due to their low detection limits and fast multi-element capability. Sample preparation is a critical step in elemental analysis, particularly when dealing with challenging matrices such as the large amounts of hydrocarbons present in petroleum (Mello et al., 2012; Sánchez et al., 2013). Sample preparation methods most frequently applied include matrix decomposition by wet digestion and dilution of the samples using organic solvents. Sample dilution is fast, simple, and can easily be automated; however, measurement of organic solutions using ICP-MS is not as straightforward as with ICP-OES, as additional problems occur, such as carbon deposition on the MS interface and carbon containing polyatomic interferences. In order to account for matrix effects, quantification of the results by standard addition (Duyck et al., 2002; Dreyfus et al., 2005), desolvation systems (Duyck et al., 2002) or ICP-SFMS (Pohl et al., 2010a, 2010b) have been applied, and oxygen can be added to the plasma gas in order to prevent carbon deposition. Viscous samples are usually analysed in highly diluted solutions in order to prevent adverse effects on aerosol generation. However, for ICP-MS analysis of petroleum and related products, wet digestion of samples is more frequently applied, resulting in aqueous sample solutions and allowing the use of aqueous standards for external calibration (Duyck et al., 2007; Sánchez et al., 2013). Preferably, digestion is carried out microwave-assisted (Wondimu et al., 2000; Dreyfus et al., 2007; Heilmann et al., 2009) or by means of a high pressure digestion system (HPA-S, Anton Paar, Graz, Austria) (Wondimu and Goessler, 2000; Ricard

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Table 1
Instrumental settings for the Agilent 8800 ICP-QQQ-MS.

	No gas	He	O_2	NH_3
MS/MS mode	Single quadrupole	Single quadrupole	MS/MS	MS/MS
RF power (W)	1550			
Sampling depth (mm)	8			
Plasma gas flow rate (l/min)	15			
Carrier gas flow rate (l/min)	0.86	0.86	0.85	0.80
Makeup gas flow rate (l/min)	0.15			
Cell gas flow rate (ml/min)	–	5.0	0.29	3.0

Table 2
Analytes and internal standards (IStd) measured in MS/MS mode using O_2 reaction gas.

Isotope	Potential interferences (May and Wiedmeyer, 1998)	Product ion	Mass shift	
			Q1	Q2
^{9}Be (IStd)	–	Be^+	9	9
^{31}P	$^{14}N^{16}O^{1}H^+$, $^{15}N^{15}N^{1}H^+$, $^{15}N^{16}O^+$, $^{14}N^{17}O^+$, $^{13}C^{18}O^+$, $^{12}C^{18}O^{1}H^+$	PO^+	31	47
^{32}S	$^{16}O_2^+$, $^{14}N^{18}O^+$, $^{15}N^{17}O^+$, $^{14}N^{17}O^{1}H^+$, $^{15}N^{16}O^{1}H^+$, $^{14}N^{16}O^{1}H_2^+$	SO^+	32	48
^{45}Sc (IStd)	$^{12}C^{16}O_2{}^{1}H^+$, $^{28}Si^{16}O^{1}H^+$, $^{29}Si^{16}O^+$, $^{14}N_2{}^{16}O^{1}H^+$, $^{13}C^{16}O_2^+$	ScO^+	45	61
^{48}Ti	$^{32}S^{16}O^+$, $^{34}S^{14}N^+$, $^{33}S^{15}N^+$, $^{14}N^{16}O^{18}O^+$, $^{14}N^{17}N_2^+$, $^{12}C_4^+$, $^{36}Ar^{12}C^+$	TiO^+	48	64
^{51}V	$^{34}S^{16}O^{1}H^+$, $^{35}Cl^{16}O^+$, $^{38}Ar^{13}C^+$, $^{36}Ar^{15}N^+$, $^{36}Ar^{14}N^{1}H^+$, $^{37}Cl^{14}N^+$, $^{36}S^{15}N^+$, $^{33}S^{18}O^+$, $^{34}S^{17}O$	VO^+	51	67
^{55}Mn	$^{40}Ar^{14}N^{1}H^+$, $^{39}K^{16}O^+$, $^{37}Cl^{18}O^+$, $^{40}Ar^{15}N^+$, $^{38}Ar^{17}O^+$, $^{36}Ar^{18}O^{1}H^+$, $^{38}Ar^{16}O^{1}H^+$, $^{37}Cl^{17}O^{1}H^+$, $^{23}Na^{32}S^+$, $^{36}Ar^{19}F^+$	MnO^+	55	71
^{75}As	$^{40}Ar^{35}Cl^+$, $^{59}Co^{16}O^+$, $^{36}Ar^{38}Ar^{1}H^+$, $^{38}Ar^{37}Cl^+$, $^{36}Ar^{39}K$, $^{43}Ca^{16}O_2$, $^{23}Na^{12}C^{40}Ar$, $^{12}C^{31}P^{16}O_2^+$	AsO^+	75	91
^{80}Se	$^{40}Ar_2^+$, $^{32}S^{16}O_3^+$	SeO^+	80	96
^{115}In (IStd)	–	In^+	115	115
^{209}Bi (IStd)	$^{193}Ir^{16}O^+$	Bi^+	209	209

Table 3
Analytes and internal standards (IStd) measured in MS/MS mode using NH_3/He reaction gas.

Isotope	Potential interferences (May and Wiedmeyer, 1998)	Product ion	Mass shift	
			Q1	Q2
^{9}Be (IStd)	–	$Be(NH_3)_4^+$	9	77
^{24}Mg	$^{12}C_2^+$	Mg^+	24	24
^{27}Al	$^{12}C^{15}N^+$, $^{13}C^{14}N^+$, $^{14}N_2$ spread, $^{1}H^{12}C^{14}N^+$	Al^+	27	27
^{39}K	$^{38}Ar^{1}H^+$	K^+	39	39
^{45}Sc (IStd)	$^{12}C^{16}O_2{}^{1}H^+$, $^{28}Si^{16}O^{1}H^+$, $^{29}Si^{16}O^+$, $^{14}N_2{}^{16}O^{1}H^+$, $^{13}C^{16}O_2^+$	$Sc(NH_3)_5^+$	45	130
^{52}Cr	$^{35}Cl^{16}O^{1}H^+$, $^{40}Ar^{12}C^+$, $^{36}Ar^{16}O^+$, $^{37}Cl^{15}N^+$, $^{34}S^{18}O^+$, $^{36}S^{16}O^+$, $^{38}Ar^{14}N^+$, $^{36}Ar^{15}N^{1}H^+$, $^{35}Cl^{17}O^+$	$Cr(NH_3)_2^+$	52	86
^{56}Fe	$^{40}Ar^{16}O^+$, $^{40}Ca^{16}O^+$, $^{40}Ar^{15}N^{1}H^+$, $^{38}Ar^{18}O^+$, $^{38}Ar^{17}O^{1}H^+$, $^{37}Cl^{18}O^{1}H^+$	$Fe(NH_3)_2^+$	56	90
^{60}Ni	$^{44}Ca^{16}O^+$, $^{23}Na^{37}Cl^+$, $^{43}Ca^{16}O^{1}H^+$	$Ni(NH_3)_3^+$	60	111
^{63}Cu	$^{31}P^{16}O_2^+$, $^{40}Ar^{23}Na^+$, $^{47}Ti^{16}O^+$, $^{23}Na^{40}Ca^+$, $^{46}Ca^{16}O^{1}H^+$, $^{36}Ar^{12}C^{14}N^{1}H^+$, $^{14}N^{12}C^{37}Cl^+$, $^{16}O^{12}C^{35}Cl^+$	$Cu(NH_3)_2^+$	63	97
^{66}Zn	$^{50}Ti^{16}O^+$, $^{34}S^{16}O_2^+$, $^{33}S^{16}O_2{}^{1}H^+$, $^{32}S^{16}O^{18}O^+$, $^{32}S^{17}O_2^+$, $^{33}S^{16}O^{17}O^+$, $^{32}S^{34}S^+$, $^{33}S_2^+$	$Zn(NH_3)_2^+$	66	100
^{115}In (IStd)	–	In^+	115	115
^{209}Bi (IStd)	$^{193}Ir^{16}O^+$	Bi^+	209	209

et al., 2011). In comparison, high pressure asher digestion is more time-consuming than microwave-assisted digestion, but allows more complete decomposition of organic matter due to higher temperatures and pressures (Wondimu and Goessler, 2000).

Even in aqueous sample solutions, the determination of elements such as phosphorus and sulfur by quadrupole-based ICP-MS is hampered by their high ionisation energies, lowering the sensitivity of their determination, and by severe polyatomic interferences (Donati et al., 2012). The ICP-MS/MS technique, also known as triple quadrupole ICP-MS (ICP-QQQ-MS), helps to overcome these limitations through its special configuration of two quadrupole mass filters on either side of an octopole-based collision/reaction cell (octopole reaction system, ORS). Therefore, not only ions exiting but also ions entering the ORS are controlled, resulting in far more predictable reactions in the cell. Typically, the first quadrupole (Q1) is set to the mass-to-charge ratio (m/z) of the target analyte ion (M^+), allowing it to reach the ORS. A reaction gas, such as O_2, can be introduced into the ORS, where it reacts with analyte ions forming oxide ions (MO^+). The second quadrupole (Q2) is set to the m/z of MO^+, allowing only the oxide ions to pass onto the detector. Interferences on the original m/z are therefore removed by Q2 (unless they also form oxides in the ORS), whilst ions interfering at the m/z of MO^+ are precluded by Q1. The described technique using different m/z settings for Q1 and Q2 is called the “mass shift” mode, as opposed to the “on mass” mode using the same m/z for Q1 and Q2. Other than O_2, NH_3 (actually 10% NH_3 in He) or H_2 can be used as reaction gases, as well as He as a collision gas. ICP-QQQ-MS has already been successfully applied to the determination of P, S, Ti, As and Se in

Table 4
Instrument detection limits (DL) and background equivalent concentrations (BEC) for analytes measured without reaction gas.

Isotope	DL (pg/g)	BEC (pg/g)
^{59}Co	3.9	5.4
^{85}Rb	0.3	2.0
^{88}Sr	0.5	3.4
^{95}Mo	23	47
^{107}Ag	0.7	2.4
^{111}Cd	0.1	0.2
^{138}Ba	3.8	20
^{185}Re	0.01	0.01
^{208}Pb	0.5	1.8
^{238}U	0.01	0.01