



Determination of P, Si and S in acid digested lubricating oil using the Agilent 8800 Triple Quadrupole ICP-MS

Application note

Petrochemical

Author

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Abstract

A new method is described for the accurate determination of silicon (Si), phosphorus (P), and sulfur (S) in lubricating oil samples using an Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ). An optimized oxygen (O_2) mass-shift method provided limits of detection for ^{28}Si , ^{31}P , ^{32}S and ^{34}S of 0.25, 0.01, 0.18 and 0.75 ppb, respectively. The method was successfully applied to the determination of Si, P and S in a lubricating oil standard reference material NIST 1848. Recoveries in the sample digests ranged from 96.4–103%.

Introduction

Due to its high sensitivity and fast multi-element capabilities, inductively coupled plasma mass spectrometry (ICP-MS) is used increasingly in chemical analysis. However, spectral overlaps from isobaric concomitant species and polyatomic ions formed in the plasma can compromise ICP-MS sensitivity and accuracy in the determination of some elements [1].



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For example, Si, P and S are difficult elements to determine at low levels by quadrupole based ICP-MS due to intense polyatomic interferences: $^{28}\text{Si}^+$, $^{31}\text{P}^+$, $^{32}\text{S}^+$ and $^{34}\text{S}^+$ suffer spectral overlaps from $^{14}\text{N}_2^+$ and $^{12}\text{C}^{16}\text{O}^+$, $^{14}\text{N}^{16}\text{OH}^+$, $^{16}\text{O}_2^+$ and $^{16}\text{O}^{18}\text{O}^+$, respectively [2]. Since the enthalpies of reaction for P^+ (-3.17 eV) and S^+ (-0.34 eV) with O_2 are negative and low for Si (0.11 eV) [3], some authors have studied the feasibility of using Collision/Reaction Cell (CRC-)ICP-MS with O_2 cell gas to determine these elements as oxide ions [4,5,6]. The method of using a reaction product ion for the detection of an element is known as mass-shift mode. Conventional CRC-ICP-MS has no control of the ions that enter the cell or the reactions that occur in the cell. In contrast, the Agilent 8800 ICP-QQQ has a tandem mass spectrometer (MS/MS) configuration with two quadrupole mass filters, Q1 and Q2, positioned either side of the Octapole Reaction System (ORS³) cell. This configuration is designed to control the reactions in the cell for more effective removal of spectral interferences (Figure 1). In mass-shift mode using O_2 cell gas, Q1 is set to the mass of the target analyte ion so only the analyte and any on-mass interfering ions can enter the ORS³ and react with the O_2 cell gas, ensuring a well controlled and more efficient reaction in the cell. The second quadrupole, Q2, is then set to the mass of the oxide ion of the element of interest, so rejecting any

interfering ions that have not reacted with the cell gas and therefore remain at the original analyte mass. Balcaen et al. evaluated the MS/MS mass-shift mode of the 8800 ICP-QQQ for the low level determination of sulfur in ethanol-diluted biodiesel samples using isotope dilution [7].

In this study, mass-shift mode was evaluated for the low level analysis of Si, P and S in lubricating oil samples. We demonstrate that the 8800 Triple Quadrupole ICP-MS operating in MS/MS mode with O_2 as the reaction gas provides low Limits of Detection (LOD) for these difficult elements and enables their accurate determination in a complex matrix such as lubricating oil.

Experimental

Instrumentation

All measurements were carried using a standard Agilent 8800 Triple Quadrupole ICP-MS (option #100). The standard configuration is composed of an x-lens, a Peltier-cooled double-pass Scott-type spray chamber, a glass concentric nebulizer, and a one-piece quartz torch with 2.5 mm internal diameter (ID) injector. Instrument operating parameters are summarized in Table 1.

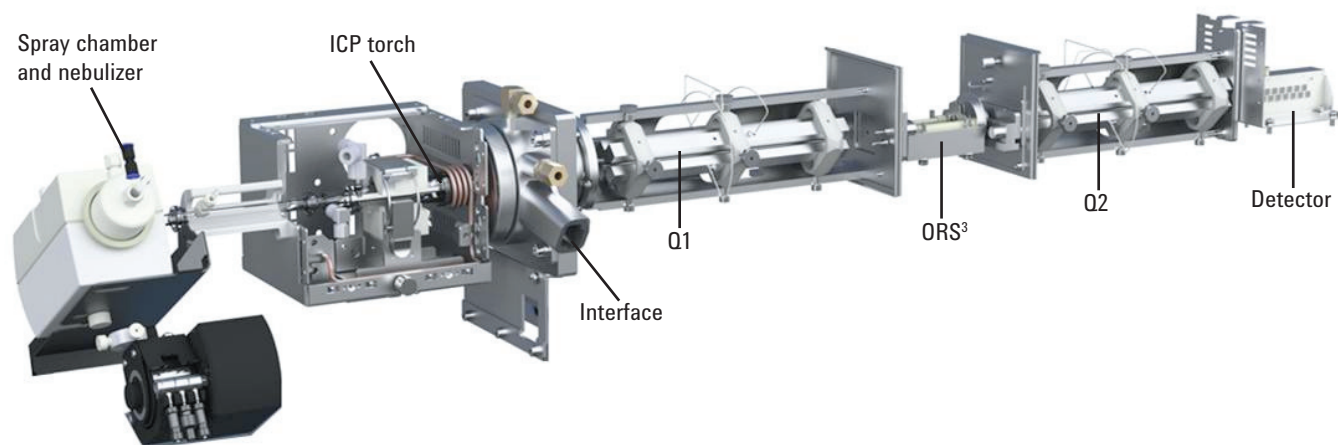


Figure 1. Schematic of the Agilent 8800 Triple Quadrupole ICP-MS

Reagents and standard solutions

Deionized water (> 18.2 MΩ cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used to prepare all solutions. Nitric acid (Merck, Darmstadt, Germany) previously purified by a sub-boiling distillation system (Milestone, Sorisole, Italy) and 30% H₂O₂ (Labsynth, Diadema, SP, Brazil) were used to digest the samples. Stock single element solutions containing 1000 mg/L of Si, P and S (Tec-Lab, Hexis, São Paulo, SP, Brazil) were used to prepare the calibration standard solutions by diluting in 1 % v/v HNO₃.

Samples and sample preparation

A lubricating oil standard reference material (SRM 1848, National Institute of Standard and Technology, Gaithersburg, MD, USA) was used to check the accuracy of the method. The SRM sample was microwave-assisted acid-digested (Milestone) using the following procedure. Aliquots of 0.25 g of the SRM 1848 were weighed directly in PTFE-PFA digestion vessels and 2.5 mL of concentrated HNO₃ was added to each flask. After standing for 30 min at room temperature, 2.5 mL of distilled–deionized water was added to the mixture. An additional pre-digestion period of 30 min without any external heating was allowed before 3.0 mL of 30% H₂O₂ was added to each digestion vessel. The

Table 1. Agilent 8800 ICP-QQQ operating conditions

Parameter	Value
RF power	1550 W
Sampling depth	8.0 mm
Carrier gas flow rate	1.08 L/min
Spray chamber temperature	2 °C
Cell gas	O ₂
Cell gas flow rate	0.5 mL/min
Mass pair (Q1, Q2)	(28, 44), (31, 47), (32, 48), (34, 50)

microwave-assisted digestion of the samples was then carried out according to the heating program presented in Table 2. The digestion flasks were allowed to cool to room temperature and then the volume of each solution was made up to 13.0 mL with distilled–deionized water. The procedure was performed in triplicate and each sample digest was diluted 200x for Si and P and 2000x for S with distilled-deionized water..

Results and discussion

Figures of merit

The analytical performance of MS/MS mass-shift mode with O₂ reaction gas was evaluated for Si, P and S. O₂ gas flow rate was optimized at 0.50 mL/min gas. Calibration curves were prepared using calibration standard solutions ranging from 0.5 to 500 ppb (Figure 2). LODs of 0.25, 0.01, 0.18 and 0.75 ppb were obtained for ²⁸Si, ³¹P, ³²S and ³⁴S respectively (Table 3) based on 10 consecutive blank measurements using the optimized acquisition conditions given in Table 1 and an integration time of 3 s.

Table 2. Heating program used in the microwave-assisted acid-digestion sample preparation procedure

Step	Applied power (W)	Time (min)	Temperature (°C)
1	250	2	80
2	0	3	80
3	550	4	120
4	650	5	180
5	750	5	200

Table 3. Limits of detection for Si, P and S obtained using the 8800 ICP-MS operating in O₂ mass-shift mode

Element	Mass pair (Q1, Q2)	Product ion	LOD (ppb)
Silicon	(28, 44)	²⁸ SiO ⁺	0.25
Phosphorus	(31, 47)	³¹ PO ⁺	0.01
Sulfur	(32, 48)	³² SO ⁺	0.18
Sulfur	(34, 50)	³⁴ SO ⁺	0.75

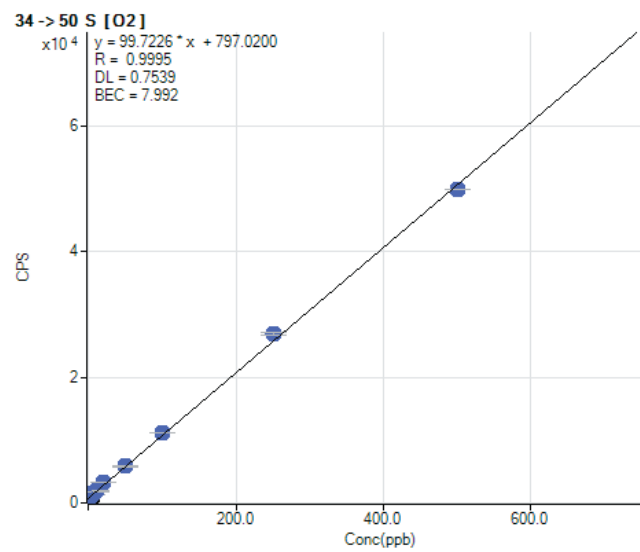
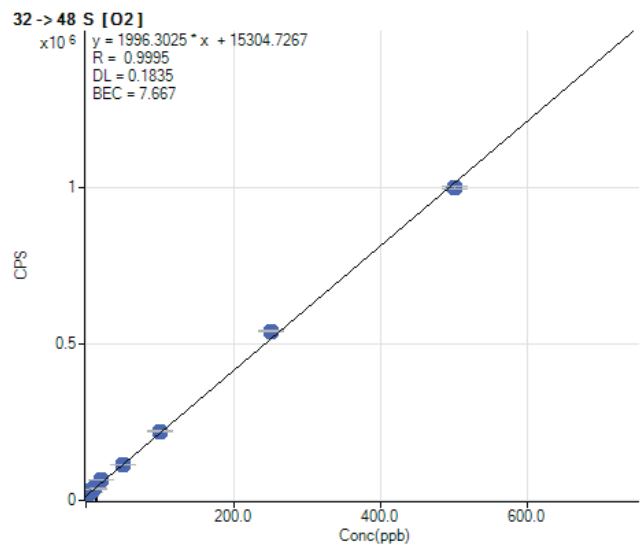
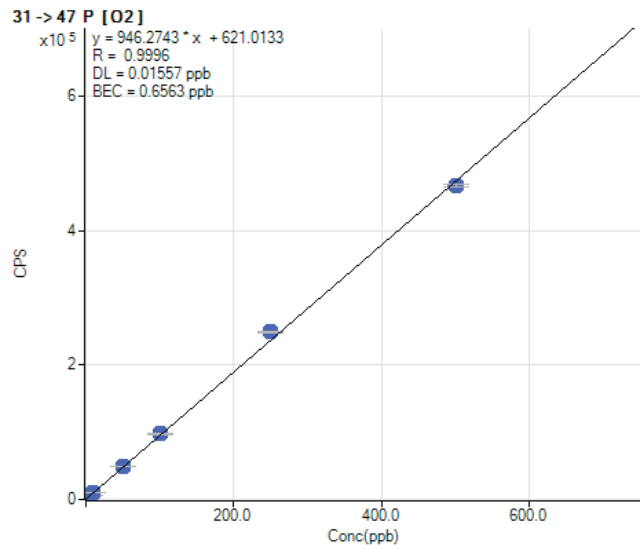
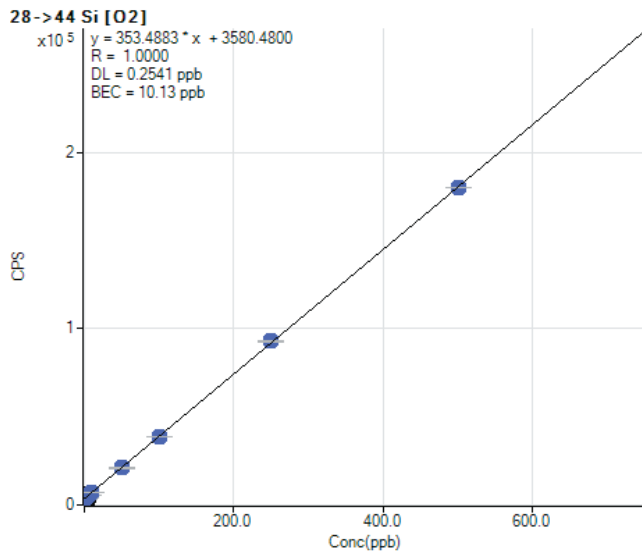


Figure 2. Calibration curves for $^{28}\text{Si}^{16}\text{O}^+$, $^{31}\text{P}^{16}\text{O}^+$, $^{32}\text{S}^{16}\text{O}^+$ and $^{34}\text{S}^{16}\text{O}^+$

Analytical application

The accuracy of the method for the determination of P, S, and Si in lubricating oil was evaluated by analyzing a digest of NIST 1848. The results are given in Table 4. The recoveries for all 3 analytes ranged from 96.4–103% indicating the effectiveness of the method to separate the analytes from the interferences. In MS/MS mode, non-target ions such as $^{44}\text{Ca}^+$, $^{48}\text{Ca}^+$, $^{47}\text{Ti}^+$, $^{48}\text{Ti}^+$ or $^{36}\text{Ar}^{12}\text{C}^+$ (that would potentially overlap with the target product ions SiO^+ , PO^+ or SO^+) are prevented from entering the ORS³ by Q1, thus allowing the accurate and sensitive determination of these difficult elements in a complex matrix.

Conclusions

The Agilent 8800 ICP-QQQ operating in MS/MS mode with oxygen cell gas effectively removes spectral interferences allowing the determination of the challenging elements Si, P and S with sub-ppb ($\mu\text{g}/\text{kg}$) LODs. By mass-shifting each of the 3 analytes by reaction with O_2 , and detecting the oxide product ions, all potential interferences from polyatomic ions based on nitrogen and oxygen are removed. Also, any ions that might overlap the analyte product ions created in the cell are rejected by Q1, greatly improving the accuracy, reliability and ease of use of reaction gas mode. Si, P and S were accurately determined in a digested lubricating oil SRM, validating the applicability of the method to the most challenging sample types.

Table 4. Results of NIST 1848 analysis

	Certified (mg/kg)	Isotope	Mass pair (Q1, Q2)	Product ion	Determined conc. (mg/kg)	Recovery (%)
Silicon	50 ^a ± 2	²⁸ Si	(28, 44)	²⁸ Si ¹⁶ O ⁺	48.2 ± 2.1	96.4
Phosphorus	7880 ± 280 ^b	³¹ P	(31, 47)	³¹ P ¹⁶ O ⁺	7650 ± 120	97.0
Sulfur	23270 ± 43 ^b	³² S	(32, 48)	³² S ¹⁶ O ⁺	24010 ± 820	103
		³⁴ S	(34, 50)	³⁴ S ¹⁶ O ⁺	23985 ± 830	103

^aReference value

^bCertified value

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