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SILICON SPECIATION IN LIGHT PETROLEUM PRODUCTS USING GAS CHROMATOGRAPHY COUPLED TO ICP-MS/MS

Raquel Sánchez,^{a,*} Fabien Chainet,^{b,*} Vincent Souchon,^b Sylvain Carbonneaux,^b Charles-Philippe Lienemann,^b José-Luis Todolí^a

Silicon speciation in light petroleum products through the hyphenation of gas chromatography coupled to ICP–tandem mass spectrometry (GC-ICP-MS/MS) is described in the present work. Eleven silicon compounds (nine siloxanes, trimethylsilanol and triethylsilane) have been taken as model molecules. The carrier and optional gas flow rates as well as the hydrogen gas flow rate in the octopole reaction cell (ORC) were critical variables. They precluded both the sensitivity and the extent of the effects caused by the sample matrix and silicon nature. The optimization of the latter variable mitigated the m/z 28 interference ($^{14}\text{N}^{14}\text{N}^+$ and $^{12}\text{C}^{16}\text{O}^+$). Moreover, under the optimized conditions, a universal response was found irrespectively of the silicon chemical form and sample matrix. The analytical performances of the method have been evaluated. Thus, the ICP-MS/MS response was linear between 0 to 500 $\mu\text{g kg}^{-1}$ with correlation coefficients up to 0.999, whereas the limit of quantification (LOQ) ranged from 8 to 60 $\mu\text{g kg}^{-1}$. Moreover, no drift was found for quality control samples analysed along a given analytical run. Only, the most volatile compound, *i.e.*, trimethylsilanol (TMSOH), induced a drop in sensitivity caused by its partial evaporation from the GC vial. The method was validated by the analysis of real samples and the results were compared with those obtained by inductively coupled plasma optical emission spectrometry (ICP-OES) and X-rays fluorescence. No significant differences in Si total content provided by the three methods were found. These results demonstrated that all silicon species were taken into account using the GC-ICP-MS/MS as speciation method. Real light petroleum products, especially coker naphtha samples, were analyzed and it was verified that they only contained cyclic siloxanes (D3-D6), mainly hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4).

1 Introduction

2 Silicon plays a crucial role in many fields such as food analysis,^{1,5}
3 semiconductor and steel industry.¹ Especially relevant is its study in
4 petroleum industry due to its poisoning effect on hydrogenation
5 catalysts during the refining process.^{2,3} In fact, silicon species are
6 adsorbed at the surface of the catalyst, thus decreasing its activity
7 with a great economic impact. Interestingly, the extent of this effect
8 depends on the chemical structure of silicon compounds.⁴⁻⁷ The
9 main source of silicon compounds is the polydimethylsiloxane
10 (PDMS) thermal degradation. This compound is usually injected
11 to enhance oil recovery (EOR) or used as an antifoaming agent during
12 refining processes.^{8,9} Among the different silicon compounds, cyclic
13 siloxanes have been identified as the major PDMS degradation
14 products with some traces of linear polysiloxanes.¹⁰ Therefore,
15 silicon speciation must be achieved in order to fully characterize

this element in hydrotreatment feeds.¹

In petroleum products total silicon concentration is at the trace level, ranging from hundreds of $\mu\text{g kg}^{-1}$ to several mg kg^{-1} .^{1,11} Therefore sensitive and accurate methods are needed to quantify this element. The most common techniques for carrying out this kind of determinations are inductively coupled plasma optical emission spectrometry (ICP-OES)^{12,13} and mass spectrometry (ICP-MS).¹⁴ However, this situation becomes more complex when speciation analysis is required. Note that a gasoline sample may contain around 200 different hydrocarbon compounds.¹¹

Several powerful analytical tools, such as normal phase high-performance liquid chromatography–mass spectrometry (HPLC-ICP-MS),¹⁴ size-exclusion ICP-MS,¹⁴ gas chromatography–mass spectrometry (GC-MS) in the single ion monitoring (SIM) mode,¹¹ Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS),¹⁵ heart-cutting gas chromatography coupled to time of flight mass spectrometry (GC-GC-TOF/MS)¹⁶ and GC-ICP-MS¹⁷ have been developed using model molecules in solvents and spiked gasolines for silicon speciation. Taking into account the limitations presented by each one of the individual techniques, Chainet *et al.*^{16,18} proposed an analytical strategy based on several techniques in order to identify the silicon species coming from synthetic PDMS

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1 degradation samples, in particular those compounds responsible 58
2 downstream catalyst poisoning in real samples. 59
3 Hyphenation of GC with a sensitive and specific detection su 60
4 as inductively coupled plasma mass spectrometry (ICP-MS) could 61
5 considered as a powerful tool for Si speciation in petroleum 62
6 products.^{1,17} However, this is not an easy task, due to the spect 63
7 interferences found at the ²⁸Si major isotope caused by ¹²C¹⁶O⁺ 64
8 organic matrices and ¹⁴N¹⁴N⁺ in a lesser extent.^{17,19} The presence of
9 carbon, together with the addition of oxygen to avoid the clogging
10 of the ICP-MS sampling cone, causes the formation of ¹²C¹⁶O⁺ and
11 degrades the sensitivity of the technique due to high background 65
12 signal.^{17,20} In order to overcome these spectral interferences, ICP 66
13 high resolution mass spectrometry (HRMS) coupled with micro-size 67
14 exclusion chromatography (μ -SEC) has been employed.¹⁸ 68
15 However, the limit of quantification was on the order of 1 mg kg⁻¹ 69
16 In a different approach, ICP high resolution mass spectrometry 70
17 (HRMS) has been coupled to normal phase-HPLC for the speciation 71
18 of standard silicon compounds in xylene.¹⁴ Two drawbacks were 72
19 found: first, it was observed that not all the silicon compounds 73
20 eluted from the column; and, second the method could not be 74
21 applied for silicon speciation in petroleum products under the 75
22 proposed chromatographic conditions. 76
23 The use of an ICP-MS equipped with a dynamic reaction cell 77
24 (DRC) has been proposed as a powerful tool to resolve polyatomic 78
25 interferences on ²⁸Si.^{22,23} NH₃ has been used as reactant gas 79
26 determine silicon traces in steels.²⁴ The presence of this 80
27 reduced the background noise signal. However, reaction between 81
28 Si⁺ and NH₃ yielding SiNH₂⁺ (m/z 44), considerably lowers the signal 82
29 on ²⁸Si.²⁵ Oxygen was demonstrated as an effective alternative 83
30 overcome spectral interferences at m/z 28 by the formation 84
31 ²⁸Si¹⁶O⁺.²⁶ Hydrogen has been used as an alternative reactant gas 85
32 Chainet *et al.*¹⁷ In this case, silicon did not react with hydrogen 86
33 whereas ¹⁴N¹⁴N⁺ and ¹²C¹⁶O⁺ did, what decreased the spectral 87
34 background noise. Although Si profiles have been obtained 88
35 acetone as solvent, the matrix effect was not studied and a non 89
36 universal response for Si compounds was observed. Very recently 90
37 Foppiano *et al.*²⁷ proposed a mixture of He and H₂ as reactant 89
38 for the determination of siloxane compounds in biogas samples. 92
39 In 2012, the introduction of a new type of quadrupole-based 93
40 ICP/MS device, the so-called ICP-tandem mass spectrometer (ICP 94
41 MS/MS) allowed the improvement of the spectral interferences 95
42 resolution by offering superior control in the cell chemistry.²⁸ The 96
43 capabilities of the ICP-MS/MS were recently demonstrated 97
44 complex organic matrices for solving interferences and reducing 98
45 detection limits.²⁹ Nelson *et al.*³⁰ applied GC-ICP-MS/MS for S, 99
46 and P detection in foods. More recently, a GC-ICP-MS/MS 100
47 instrumental setup was successfully developed for 101
48 determination of the content of sulfur and its species in gasoline.³¹ 102
49 In 2020, Radermacher *et al.*³² proposed the GC-ICP-MS/MS coupled 103
50 for cyclic volatile methylsiloxanes determination in fish samples 104
51 after a solid-liquid extraction procedure. However, to our 105
52 knowledge, the potential of GC-ICP-MS/MS for the direct speciation 106
53 of a difficult element like Si in complex matrices without 107
54 previous extraction method has not been reported yet in 108
55 literature. The aim of the present work was thus to develop a 109
56 ICP-MS/MS method for silicon speciation in light petroleum 110
57 products. First GC-ICP-MS/MS optimization was carried out using

hydrogen as reactant gas. It allowed successful detection of silicon
with a complete resolution of interferences. One of the main goals
of the present work was to develop a method in which the
influence of the matrix nature and the silicon chemical form on
sensitivity was minimized. Once the analytical figures of merit were
evaluated, the method was validated and applied to the analysis of
real light petroleum products.

Experimental

Standard solutions and samples

Silicon standards. A test mixture of eleven silicon model
compounds was used in this work. Siloxanes (cyclic and linear),
silanols and silanes were selected based on their identification in
synthetic PDMS degradation samples¹⁶ and thus, on their possible
presence in petroleum products:^{3,17} trimethylsilanol (*TMSOH*, b.p
98°C); pentamethyldisiloxane (*A*, b.p 80°C); hexamethyldisiloxane
(*L2*, b.p 100°C); triethylsilane (*F*, b.p 107°C);
hexamethylcyclotrisiloxane (*D3*, b.p 134°C); octamethyltrisiloxane
(*L3*, b.p 153°C); octamethylcyclotetrasiloxane (*D4*, b.p 175°C);
decamethyltetrasiloxane (*L4*, b.p 194°C);
decamethylcyclopentasiloxane (*D5*, b.p 211°C);
dodecamethylpentasiloxane (*L5*, b.p 210°C);
dodecamethylcyclohexasiloxane (*D6*, b.p 245°C).
Tetrakis(trimethylsilyloxy)silane (*M4Q*, b.p 106°C) was used as
internal standard to consider density difference between heptane
and real samples as well as potential sample evaporation during the
analysis (more details in "Analytical figures of merit and method
validation" section). Individual standards of silicon compounds were
purchased from Sigma-Aldrich (L'Isle d'Abeau, France) and
Interchim (Montluçon, France). A mixture of these silicon
compounds was prepared in heptane (VWR, quality Normapur,
Fontenay sous Bois, France). Different dilutions were prepared to
calculate quantification limits and to build the calibration curves.
Specific vials in polypropylene with septa caps only made of PTFE
provided by VWR (Fontenay sous Bois, France) in replacement of
classical septa made of silicones to avoid cyclic siloxane
contaminations were used. More details on the complete analytical
procedure for Si speciation were already reported in Chainet *et al.*^{11,15}
to avoid potential contaminations and artifacts.

Samples. Two gasolines without silicon, one from direct distillation
of crude oil (Straight-Run Gasoline) and the other from fluid
catalytic cracking (FCC Gasoline) were used to evaluate matrix
effects. One reforming naphtha (Naphtha), without silicon was
analyzed as quality control (QC) after spiking it with model silicon
compounds at around 250 $\mu\text{g kg}^{-1}$. Three coker naphthas (coker
naphthas A, B and C) originated from different refineries were also
studied. Note that coking is a refining process based on thermal
cracking at 500 °C of heavy petroleum products into lighter cuts
(diesel or naphtha). PDMS is generally used as antifoaming to
minimize the generation of emulsions in this process. Table 1

1 **Table 1.** Physicochemical characteristics of the samples analyzed.

Properties	Methods	Gasolines			Coker naphthas		
		Straight-Run Gasoline	FCC Gasoline	Reforming Naphtha	A	B	C
Density (g cm ⁻³)	NF EN ISO 12185	0.7481	0.6820	0.7422	0.7735	0.7635	0.7241
Boiling range (°C)	IFPEN 9302	23-230	23-107	74-158	69-219	0-294	0-208
Sulphur concentration (mg kg ⁻¹)	NF ISO 20884	385	587	<0.3	12192	9810	5632
Nitrogen concentration (mg kg ⁻¹)	ASTM D4629	40.1	0.44	<0.3	133	206	103
RON [#]	IFPEN 9302	90.4	64	Nd	66	nd	67
n-Paraffins concentration (%wt)		48.9	39.10	27.39	19.92	nd	29.45
Isoparaffins concentration (%wt)			36.71	28.99	0.92	nd	1.90
Naphtens concentration (%wt)			19.98	30.48	8.65	nd	9.30
Aromatics concentration (%wt)		26.1	4.13	13.15	34.24	16.87*	28.4
Olefins concentration (%wt)		25	0.07	Absent	18.2	nd	12.6

nd: not determined; *Determined by UV method; [#] RON: research octane number

2 summarizes the samples provided by IFP Energies Nouvelle
3 (Solaize, France) and their characteristics determined by standard
4 methods for density, sulfur, and nitrogen concentration and by test
5 IFPEN 9302³³ internal method for boiling range and hydrocarbon
6 composition.

8 Instrumentation

9
10 **GC-ICP-MS/MS apparatus.** All measurements were carried out
11 using an Agilent 7890B GC (Agilent Technologies, USA) coupled
12 an Agilent 8800 ICP-QQQ instrument (Agilent Technologies, CA,
13 USA) using an Agilent GC-ICP-MS transfer line (Agilent Technologies,
14 Japan). The GC-ICP-MS interface consists of a passivated transfer
15 line (sulfinert) with an injector tube both heated at 300°C and a
16 special torch. The GC column was connected *via* a T piece to the
17 pre-heating pipe for supplying the argon carrier gas in order to
18 sweep the GC column effluents through the transfer line into the
19 plasma. In this way, the sample was maintained at a constant high
20 temperature from the end of the chromatographic column in the
21 GC oven to the tip of the ICP injector. Using the electronic
22 pneumatic control (EPC) module, a mixture argon/oxygen (80/20)
23 as optional gas (OG) was added to the Ar carrier gas to burn off
24 carbon deposits coming from the samples. A mixture of Xe at 0.1%
25 in He (Air liquide, France) was used as an alternate GC carrier gas to
26 tune the ICP-MS/MS (resolution and mass axis) for the maximum of
27 sensitivity on the ¹²⁴Xe m/z value. Using the ICP-MS/MS for Si, Q1
28 and Q2 were set to m/z 28 because there was no reaction with H₂ in
29 the cell.¹⁷ However, the main interferences of concern, ¹⁴N¹⁴N⁺ and
30 ¹²C¹⁶O⁺ reacted with H₂ to form respectively ¹⁴N¹⁴N¹H⁺ and
31 ¹²C¹⁶O¹H⁺ (m/z 29) and were minimized by Q2 set at 28. More
32 details on the operating conditions of the GC-ICP-MS/MS system
33 are listed in Table 2.

34

ICP-OES apparatus. An Optima 7300 DV Perkin-Elmer ICP-OES
spectrometer (Uberlingen, Germany) was used to determine total Si
at trace levels and the emission signals were axially taken. A
concentric micronebulizer fitted to the high temperature Torch
Integrated Sample Introduction System (hTISIS) was used as sample
introduction system.¹² The hTISIS temperature was set at 400°C and
the sample was aspirated at 30 μL min⁻¹ according to an air
segmented injection regime.³⁴ The solutions were delivered to the
nebulizer by means of a peristaltic pump (Perimax 16 antiplus,
Spetec, Erding, Germany) and a 0.19-mm id flared end PVC-based
tubing (Glass Expansion, Melbourne, Australia) was employed.

XRF apparatus. The total Silicon content was also determined
following an internal IFPEN method.³⁵ A Panalytical Axios (Almelo,
Netherlands) 4 kW equipped with a Cr anode was used to perform
the wavelength dispersive X-rays fluorescence (WDXRF) analysis. A
2 mL minimum solution volume was introduced within a cup with a
polypropylene 6 μm film. The quantification limit was 10 mg kg⁻¹ of
Si with a measuring time of 30 seconds to avoid the evaporation of
the light petroleum products.

Table 2. Operating conditions of the GC-ICP-MS/MS system.

GC Conditions	
Injection	1μL in Split 1:10 mode at 280°C through a Merlin Microseal system
Carrier gas	He at 2 mL min ⁻¹
Column	DB-5 MS UI (30mx0.25mmx0.25μm)
Oven program temperature	35°C (5min) → 140°C at 10°C min ⁻¹ → 250°C at 20°C min ⁻¹
Transfer line and Injector temperature	300°C
ICP-MS/MS detection conditions (<i>optimized conditions in italics</i>)	
Cones Type	Pt cones
Sample depth	8 mm.
RF Power	1550 watts

Carrier gas flow (CG)	Ar at 0.4-0.8 L min ⁻¹ (0.5 L min ⁻¹)	35
Optional gas flow (OG)	Ar/O ₂ (80/20) at 0-0.25 L min ⁻¹ (0.15 L min ⁻¹)	36
ORC Gas flow	H ₂ at 0-3.0 mL min ⁻¹ (2 mL min ⁻¹)	37
Isotopes monitored	²⁸ Si → ²⁸ Si	38
Q1 → Q2	¹³ C → ¹³ C; ³⁷ ArH → ³⁷ ArH;	39
	³⁸ Ar → ³⁸ Ar	40

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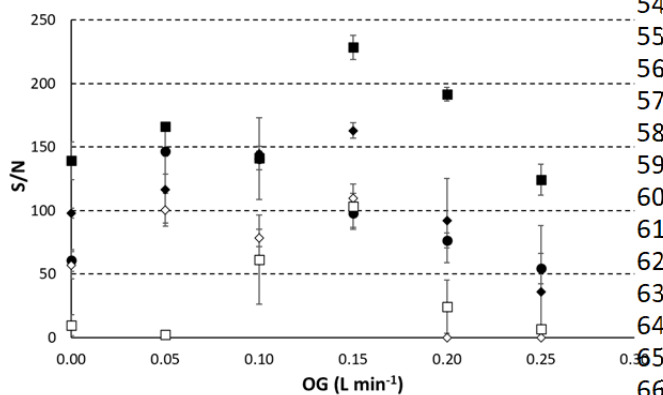
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2 Results and discussion

4 Optimization of the GC-ICP-MS/MS operating parameters

5 A 1 mg kg⁻¹ solution of octamethylcyclotetrasiloxane (D4) 49
6 heptane was taken as a model because it (and D3) was the most 50
7 recovered compound in synthetic PDMS degradation samples 51
8 Furthermore, its boiling point is close to those for real naphtha 52
9 samples. Therefore, this compound was used both for the 53
10 optimization of the carrier (CG), optional (OG) and hydrogen gas 54
11 flow rates.

12 **Optimization of the carrier gas and optional gas flow rates.** As 54
13 Figure 1 shows, the highest signal to noise ratio values were 55
14 obtained for a CG equal to 0.5 L min⁻¹ and an OG of 0.15 L min⁻¹. For 56
15 carrier gas flow rates higher than 0.6 L min⁻¹, the S/N ratio dropped 57
16 and the reproducibility became poor. This could be explained by a 58
17 degradation of the thermal characteristics of the plasma caused by 59
18 the increase in the total gas plasma load.



20 **Figure 1.** Signal-to-noise ratio (S/N) for D4 as a function of the 67
21 carrier (CG) and optional (OG) gas flow rates. Carrier gas flow rates 68
22 0.4 L min⁻¹ (black circles); 0.5 L min⁻¹ (black squares); 0.6 L min⁻¹ 69
23 (black diamonds); 0.7 L min⁻¹ (white diamonds); 0.8 L min⁻¹ (white 70
24 squares). H₂ gas flow rate: 0.5 mL min⁻¹. The values corresponded 71
25 the average ± standard deviation (3 replicates were measured). 72

26 Taking into account that the optional gas consisted of a mixture 74
27 of Ar/O₂ (80/20), under optimum conditions (CG = 0.5 L min⁻¹; OG = 75
28 0.15 L min⁻¹) the oxygen gas flow rate represented 6% of the total 76
29 gas introduced into the plasma. The amount of O₂ added under 77
30 these conditions was enough for the complete conversion of C to 78
31 CO, thus avoiding the carbon soot deposits in the cones. Plasma 79
32 degradation could be evaluated by following the signal of the 80
33 isotope. Figure 2 shows the superimposition of the 81

chromatogram and the evolution of ³⁸Ar signal with time for two 82
different situations: (i) the optimal values of carrier and optional gas 83
flow rates in terms of S/N; and, (ii) values of carrier and optional gas 84
flow rates equal to 0.4 L min⁻¹ and 0.1 L min⁻¹, respectively. For a 85
given set of operating conditions, two peaks were found. A first one 86
appearing at around 1.9 min that corresponded to heptane and a 87
second one that was due to the elution of the D4 silicon compound 88
at approximately 2.5 min. The former peak was found at a 28 m/z 89
ratio (see dashed lines in Figure 2) since only 0.5 mL min⁻¹ of 90
hydrogen were added to the cell (fixed value before the ORC 91
optimization). Therefore, this peak revealed the magnitude of the 92
interference of ¹²C¹⁶O⁺ that, as expected, was more intense for the 93
optimum conditions than when the total gas flow (CG+OG) was 94
lower. It should also be mentioned that when heptane arrived to 95
the plasma, the ³⁸Ar signal decreased (Figure 2) by roughly a 20% 96
and 75% for CG=0.4 L min⁻¹ and OG=0.1 L min⁻¹ and optimal 97
conditions, respectively, that demonstrated the detrimental impact 98
of the solvent on the plasma ionization characteristics. (Figure 2).

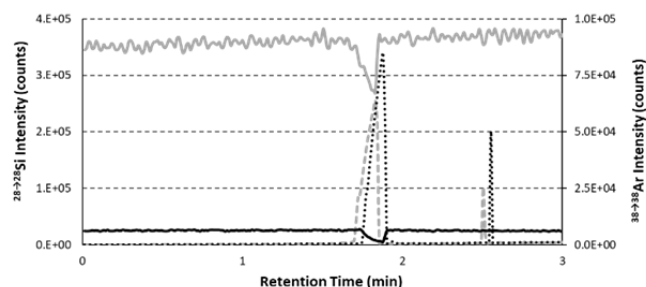
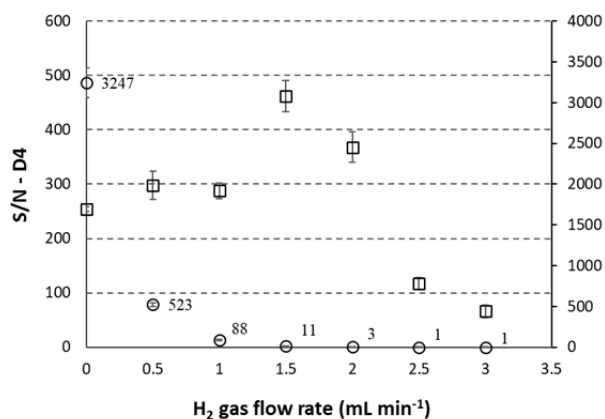


Figure 2. ²⁸Si (dashed lines) and ³⁸Ar (continuous lines) 99
chromatogram for the D4 at 1 mg kg⁻¹ in heptane. Grey: carrier and 100
optional gas flow rate: 0.4 L min⁻¹ and 0.10 L min⁻¹; black: 0.5 L min⁻¹ 101
and 0.15 L min⁻¹. H₂ gas flow rate: 0.5 mL min⁻¹.

Optimization of the octopole reaction cell (ORC). When 102
experiments were performed before the optimization of the ORC, 103
the heptane peak at m/z 28 due to the ¹²C¹⁶O⁺ interference was 104
observed (Figure 2). With the injection of up to 2 mL min⁻¹ of H₂, the 105
¹²C¹⁶O⁺ interference was minimized without any degradation in 106
sensitivity. To illustrate the H₂ optimization, GC-ICP-MS/MS 107
chromatograms are available in Figure S1. For example, a 108
diminution of the heptane peak intensity by a factor of 30000 when 109
switching from 0.5 to 2 mL min⁻¹ of H₂ was observed, whereas a 110
diminution factor of 16 was found for D4 (Figure S1). As Figure 3 111
shows, for this silicon compound, the signal to noise ratio (S/N) was 112
not drastically affected, because the standard deviation of the 113
background noise decreased with the H₂ gas flow rate. The highest 114
D4 signal to noise ratio was obtained for the 1.5 mL min⁻¹, however 115
at this flow rate a ¹²C¹⁶O⁺ interference due to the heptane was still 116
observed (Figure 3 and Figure S1). For that reason, 2.0 mL min⁻¹ of 117
H₂ was selected as optimum value, as it represented a compromise 118
between the S/N ratio and the minimization of the ¹²C¹⁶O⁺ 119
interference. At flow rates higher than 2.0 mL min⁻¹, the S/N was 120
drastically reduced. In fact, at 3.0 mL min⁻¹ the D4 peak height 121
decreased by a factor of 180 (Figure 1S).

1



2 **Figure 3.** Signal-to-noise ratio (S/N) for D4 and heptane as a
 3 function of the hydrogen flow rate. Carrier gas flow rate: 0.5 L min⁻¹;
 4 optional gas flow rate: 0.15 L min⁻¹. The values corresponded
 5 to the average \pm standard deviation (3 replicates were measured).
 6 Circles: heptane; squares: D4.

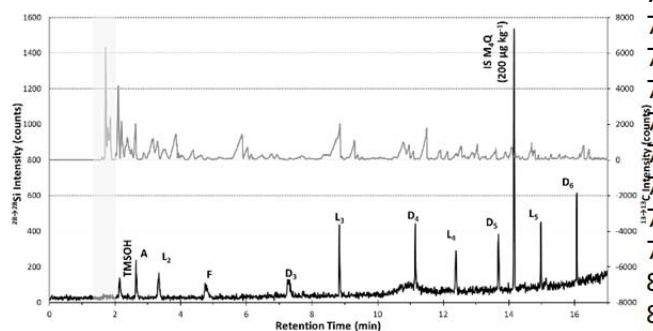
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8 Analytical performances and validation of GC-ICP-MS/MS method

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10 **Separation of silicon compounds in a spiked sample.** A sample of
 11 FCC gasoline was spiked with the mixture containing 50 $\mu\text{g kg}^{-1}$ of
 12 the silicon model compounds and analyzed by GC-ICP-MS/MS under
 13 the optimized conditions. Figure 4 shows the evolution of ¹³C with
 14 time together with the chromatogram for ²⁸Si obtained for this
 15 sample. It can be verified that the matrix did not cause any
 16 distinguishable peak in the chromatogram obtained for silicon (see
 17 grey area in Figure 4). The signal recording for ¹³C corresponded to
 18 non-silicon containing organic compounds. As it may be observed
 19 there was a mismatching between the ²⁸Si peaks and those for
 20 carbon. The overcoming of the interference of ¹²C¹⁶O⁺ allowed to
 21 determine all the injected silicon compounds (even the most
 22 volatile ones such as TMSOH) at a concentration as low as 50 $\mu\text{g kg}^{-1}$
 23 of Si.

24



25 **Figure 4.** GC-ICP-MS/MS chromatograms of the 50 $\mu\text{g kg}^{-1}$ spiked
 26 FCC gasoline. Grey line: ¹³C; black line: ²⁸Si. Carrier gas flow rate: 0.5
 27 L min⁻¹; optional gas flow rate: 0.15 L min⁻¹, H₂ gas flow rate: 2.0 mL
 28 min⁻¹.

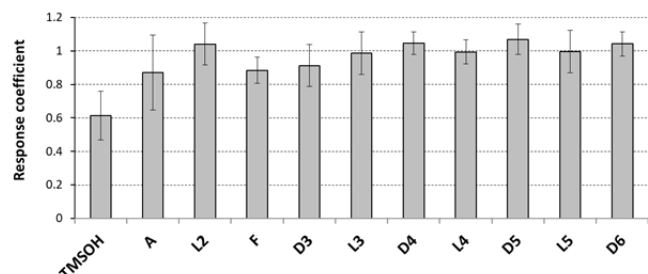
29
 30 **Sample matrix and silicon chemical form effect.** Calibration curves
 31 ranging from 0 to 500 $\mu\text{g kg}^{-1}$ were prepared with the eleven silicon

32 compounds in three different matrices: heptane (two calibration
 33 curves were prepared in different days), and two gasolines without
 34 silicon-containing compounds (a straight-run gasoline and a FCC
 35 gasoline, with different physico-chemical characteristics (Table 1)).
 36 Calibration curves ($y = ax$) for each compound (C) were calculated,
 37 where y corresponded to $\frac{\text{Area C}}{\text{Area IS}}$ and x was the $\frac{\text{Concentration C}}{\text{Concentration IS}}$
 38 ratio. IS refers to the internal standard M4Q added in both calibration
 39 samples at a precisely known concentration around 250 $\mu\text{g kg}^{-1}$ of
 40 silicon.

41 In order to evaluate the effect of the matrix on the analytical
 42 response, the slopes of the calibration curves were considered in
 43 relative terms. Thus, for each silicon model molecule, the slope
 44 obtained for the calibration curve prepared by using each gasoline
 45 and one of the replicates of the heptane was divided by that
 46 obtained for the second replicate of heptane. The relative slopes
 47 were close to unity regardless of the Si compound (Figure S2). The
 48 variation between the slopes was less than 10%, except for the
 49 most volatile compounds. In fact, the values of the slopes obtained
 50 for TMSOH were 15-20% higher when the FCC gasoline and heptane
 51 samples were analyzed than in the case of the straight-run gasoline
 52 (Figure S2). Meanwhile, the slope ratio in the case of compound A
 53 also deviated significantly from the unity when analyzing the
 54 straight-run gasoline. This could be explained by the evaporation of
 55 the silicon compounds over the time, as the second replicate for
 56 heptane was taken as reference. In any case, globally speaking,
 57 these results revealed that under the optimal conditions, matrix
 58 effects were mitigated (Figure S2).

59 Contrarily to what Chainet *et al.*¹⁷ and Grümping *et al.*³⁶
 60 observed, in the present work, a virtually universal response was
 61 found for all silicon compounds (Figure 5). One of the hypotheses to
 62 explain the non-universal response in previous reports was the
 63 addition of cold argon (22 °C) at the exit of the GC column, thus
 64 causing a cold point in the transfer line and a potential decrease in
 65 the transfer efficiency to the ICP-MS for some silicon species.¹⁷ To
 66 overcome this problem, the temperature of the transfer line was
 67 set to 300°C and the cold argon was pre-heated in the oven of the
 68 GC before injection. As Sánchez *et al.*^{12,37} demonstrated using a
 69 total sample consumption system heated at 350°C, the so-called
 70 hTISIS allowed to minimize the effect of the silicon chemical form
 71 and the matrix on the ICP-signal. In the present work, the average
 72 and the confidence interval (as 3 x standard deviation) of the slope
 73 obtained in the different matrices and different days for each silicon
 74 compound were calculated. Thus, the slope corresponded to the
 75 response coefficient of each silicon compound and was equal by
 76 definition to the unity for the IS. As Figure 5 shows, the GC-ICP-
 77 MS/MS response was similar irrespectively of the silicon chemical
 78 form, except for the most volatile compound, trimethylsilanol
 79 (TMSOH) and pentamethyldisiloxane (A). The confidence interval is
 80 around 20% for these volatile compounds but less than 13% for the
 81 others. Similarly to the findings in the Chainet *et al.* work,¹⁷ TMSOH
 82 presented a lower response. As the calibration curve for TMSOH
 83 was linear ($R^2=0.9965$), the lower response observed was probably
 84 due to the evaporation of this compound regarding its volatility.
 85 This hypothesis was evaluated by the introduction of quality control
 86 samples (QC) over the analytical run. The QC samples were
 87 prepared by spiking the reforming naphtha (Table 1) at 250 $\mu\text{g kg}^{-1}$
 88 level with the Si test mixture. As Figure S3 shows, recovery for the

1 most volatile compounds, especially for TMSOH, decreased over time. This parameter went from approximately 112 to 60%, thus proving the evaporation from the vial of this compound. Similar behavior was found for the compound A, but in this case the recovery values decreased by a factor of 20% over the time (Figure S3). Therefore, the influence of the silicon chemical form sensitivity was not caused by an instrumental bias.



9 **Figure 5.** Response coefficients for each silicon compound obtained using GC-ICP-MS/MS related to IS. Carrier gas flow rate: 0.5 L min⁻¹, optional gas flow rate: 0.15 L min⁻¹, H₂ gas flow rate: 2.0 mL min⁻¹. The value was represented as average ± confidence interval (four calibration curves were measured).

15 **Analytical figures of merit and method validation.** One of the challenges to achieve a good peak definition and, thus, repeatability in GC-ICP-MS/MS is the need for a compromise between the number of points per peak and the signal to noise ratio. Repeatability of the method was evaluated by obtaining three replicates of the chromatograms for a 1 mg kg⁻¹ solution of prepared in heptane at different dwell times. At the highest value of dwell time the peak was poorly defined, thus degrading the repeatability of the method. The relative standard deviation of the peak area was approximately 10%. The highest signal to noise ratio was obtained for a dwell time equal to 0.2 s. However, the maximum number of points per peak and the lowest relative standard deviation of the peak area values were obtained at 0.1 s dwell time. Therefore, the latter value was taken as the optimum one.

30 One of the most relevant analytical figures of merit is the limit of quantification (LOQ). The determinations of the limit of detection (LOD) and LOQ are based on the calculation of 3 and 10 times the absolute standard deviation of the background, respectively.³⁸ In the present work, the minimum concentration that can be

accurately measured by GC-ICP-MS/MS according to the described quantification method was determined. Spiked heptane and gasoline solutions, considered now as samples, were analyzed using a heptane calibration curve prepared in a different day. An acceptable confidence interval of 20% between the known and the experimentally determined concentration was chosen to validate the LOQ. The results revealed that this parameter ranged from 8 to 60 µg kg⁻¹, except for the three most volatile compounds (TMSOH, A and L2) in heptane (Table 3). The obtained LOQ in the case of L2 in heptane was likely due to its peak shape distortion induced by the high amount of heptane leaving the GC capillary phase at the same retention time. This chromatographic issue was not observed in gasolines. Quantification limits were compared with the previous values obtained by Chainet *et al.*¹⁷ Under optimized conditions, the GC-ICP-MS/MS method presented lower LOQ values than those obtained in the previous work. The improvement factor ranged from 2 to 28, depending on the silicon compound.

The linearity of the GC-ICP-MS/MS was studied for a concentration range from 0 to 500 µg kg⁻¹ of silicon in heptane. The ICP-MS/MS response was linear with correlation coefficients up to 0.999. Method applicability was tested by measuring six quality control standards (QC) distributed throughout the analytical run to assess a possible drift in the analytical signals. They were prepared by spiking one reforming naphtha (Table 1) at 250 µg kg⁻¹ level with a Si test mixture. For the family of cyclic siloxanes (D3, D4, D5 and D6), calculated recovery values ranged from 92-109%; whereas for the remaining silicon compounds the recoveries were in the 80-120% range, except for TMSOH. In this case, recovery decreased over the analytical run (Figure S3). This behavior could be explained by TMSOH evaporation from the vial with time. Note that TMSOH was the most volatile silicon compound. Regression analysis³⁹ of QC data were performed and no systematic trends at 95% of confidence level were visible, except for trimethylsilanol (TMSOH). These results clearly validated the GC-ICP-MS/MS method for the Si speciation in light petroleum products and could be applied to real coker naphtha samples.

Analysis of real coker naphtha samples

For speciation analysis, coker naphthas were diluted in heptane to fit the calibration curve range from 0 to 500 µg kg⁻¹. The GC-ICP-

77 **Table 3.** Limit of quantification (LOQ) (µg kg⁻¹) and retention time (min) obtained for each silicon compound.

Silicon compound	Retention time (min)		Limit of quantification (µg kg ⁻¹)		
	Heptane	Straight-run Gasoline	FCC Gasoline	Acetone Chainet ¹⁷	
TMSOH	2.15	80	44	24	57
A	2.62	77	43	18	nc
L2	3.27	177	8	8	77
F	4.70	8	8	8	227
D3	7.20	49	25	25	85
L3	8.70	12	31	55	112
D4	11.04	49	49	49	112
L4	12.31	44	10	44	110
D5	13.63	47	47	47	83
L5	14.94	24	24	24	78
D6	16.02	33	58	58	63

nc: not considered

Table 4. Silicon species and total Si concentration (mg kg^{-1}) obtained by GC-ICP-MS/MS^a, ICP-OES^a and XRF^b.

Coker Naphtha	Dilution factor	D3	D4	D5	D6	Total GC-ICP-MS/MS	Total hTISIS-ICP-OES	Total XRF
A	70	9.0 ± 0.3	6.0 ± 0.4	2.7 ± 0.4	1.27 ± 0.10	20.0 ± 1.3	19.9 ± 1.4	19 ± 10
B	20	0.89 ± 0.14	0.36 ± 0.10	nd	nd	1.3 ± 0.2	1.55 ± 0.14	<10
C	80	5.2 ± 0.2	2.5 ± 0.9	nd	nd	8.0 ± 0.7	7.6 ± 0.6	<10

nd: not detected; ^aThe values corresponded to the average $\pm 3 \times$ standard deviation (3 replicates); ^bThe values were the average \pm method confident interval (2 replicates)

MS/MS chromatogram obtained for the coker naphtha A is illustrated in Figure 6. Four cyclic siloxanes D3-D6 were identified according to their retention times (Table 3) and quantified on the sample. One unknown silicon peak, likely coming from the column bleeding was also present at around 15 minutes. This peak was also detected in blanks and QC but it did not overlap with the analytes. GC-ICP-MS/MS chromatograms of coker naphthas B and C are also illustrated in Figure S4. No other silicon compound was detected in the three coker naphthas. These results confirmed that cyclic siloxanes (Dn) were the main PDMS thermal degradation compounds in synthetic PDMS degradation samples¹⁷ and real naphthas,³ oil and gas process conditions could clearly influence the formation of other silicon compounds but at very low levels compared to cyclic siloxanes.

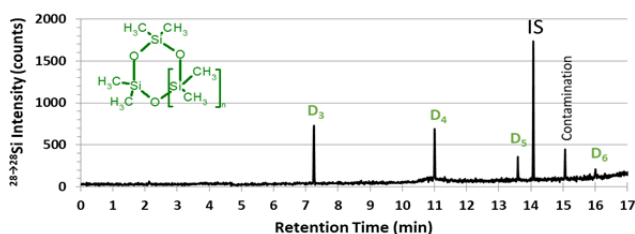


Figure 6. GC-ICP-MS chromatogram of the coker naphtha A sample (IS: internal standard). Carrier gas flow rate: 0.5 L min^{-1} , optional gas flow rate: 0.15 L min^{-1} , H_2 gas flow rate: 2.0 mL min^{-1} .

To validate the speciation method by GC-ICP-MS/MS, we must verify that all silicon species are identified and quantified. As no certified reference materials exist for Si speciation in petroleum products, the sum of the concentrations of Si species was compared to the total Si content. Total silicon concentration was determined by XRF and ICP-OES, especially for low Si concentration, and then compared to the GC-ICP-MS/MS results for the validation of the method. Table 4 reveals that there were no differences between the total Si concentration in coker naphtha A for the three employed methods (coefficient of variation less than 3%). The coefficient of variation between the GC-ICP-MS/MS and ICP-OES results for coker naphthas B and C, with total Si content below the XRF LOQ, were respectively lower than 12% and 4%. These results demonstrated that all silicon species were properly identified and quantified. Therefore, the developed GC-ICP-MS/MS was validated for silicon speciation in petroleum samples.

Conclusions

The main goal of this work was to develop a method for silicon speciation in light petroleum products based on GC-ICP-MS/MS. The main concern of ²⁸Si determination by ICP-MS related with the spectral interferences due to the formation of ¹²C¹⁶O⁺ and ¹⁴N¹⁴N⁺ has been eliminated by adding hydrogen as reactant gas in the octopole reaction cell (ORC). The optimization of the GC-ICP-MS/MS operating parameters (carrier gas, optional gas and hydrogen gas flow rates) plays a crucial role to obtain a detector response independently of sample matrix and silicon chemical form. Moreover, LOQ values ranged from 8 to $60 \mu\text{g kg}^{-1}$.

GC-ICP-MS/MS method has been validated by the analysis of different petroleum derivatives. Cyclic siloxanes (D3-D6) were confirmed as the main silicon compounds present in coker naphtha samples. The proposed GC-ICP-MS/MS and two alternative analytical methods (ICP-OES and XRF) have provided similar total Si concentrations and have demonstrated that all silicon species have been taken into account. Therefore, the new method could be applied to the determination of Si catalyst contaminants in light petroleum products. The achievement of silicon speciation in real coker naphthas will allow the development of trapping systems to remove these compounds before hydrotreatment catalysts.

Conflicts of interest

There are no conflicts to declare.

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