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par

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Sujet de la thèse

SPÉCIATION DU SILICIUM DANS LES CHARGES D'HYDROTRAITEMENT

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Sommaire

Liste des communications

Articles scientifiques :

-Silicon speciation by hyphenated techniques in environmental, biological and industrial issues : a review, F. Chainet, C-P. Lienemann, M. Courtiade, J. Ponthus, O-F-X. Donard, **J. Anal. At. Spectrom.**, 2011, 26, 30

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-Characterization of silicon species issued from PDMS degradation under thermal cracking of hydrocarbons: Part 1-Gas samples analysis by gas chromatography-mass spectrometry, F. Chainet, L. Le Meur, C-P. Lienemann, M. Courtiade, J. Ponthus, O-F-X. Donard, **Fuel**, 2012 (Soumis)

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Ces articles scientifiques constituent la base de ce travail et sont reportés dans les différents chapitres suivant l'ordre d'apparition proposée ci-dessus.

Communications orales :

-Spéciation des composés silicés par GC/MS appliquée aux produits pétroliers, F. Chainet, C-P. Lienemann, M. Courtiade, J. Ponthus, O-F-X. Donard, **Journée du Club Jeunes AFSEP**, 14 octobre 2010, (Paris)

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-Spéciation des composés silicés dans les produits pétroliers par Chromatographie en phase Gazeuse couplée à la Spectrométrie de Masse (GC/MS), F. Chainet, C-P. Lienemann, M. Courtiade, J. Ponthus, O-F-X. Donard, **27èmes Journées Françaises de Spectrométrie de Masse**, 13-16 Septembre 2010 (Clermont-Ferrand)

-Identification of silicon compounds in gasolines by FT-ICR/MS: Towards the speciation by Kendrick plot, F. Chainet, J. Ponthus, C-P. Lienemann, M. Courtiade, O-F-X. Donard, **ASMS 11**, 4-10 juin 2011, (Denver, Colorado, États-Unis)

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-Silicon speciation in petroleum products using a multi-technical approach by Mass Spectrometry (MS) for a better understanding of catalyst poisoning, F. Chainet, J. Ponthus, C-P. Lienemann, M. Courtiade, O-F-X. Donard, **19th IMSC**, 15-21 Septembre 2012, (Kyoto, Japon)

Liste des abréviations

AAS : Spectroscopie d’absorption atomique (Atomic Absorption Spectroscopy)
AED : Détecteur à émission atomique (Atomic Emission Detector)
APCI : Ionisation chimique à pression atmosphérique (Atmospheric Pressure Chemical Ioniztion)
BEC : Concentration équivalente du bruit de fond (Background Equivalent Concentration)
BP : Point d'ébullition (Boiling Point)
BTX : Benzène, Toluène, Xylène
DBE : Double liaison équivalente (Double Bond Equivalent)
d-DIHEN : Nébuliseur à injection directe haute efficacité (demountable Direct Injection High Efficiency Nebulizer)
DRC : Cellule de collision réaction (Dynamic Reaction Cell)
DS : Deans Switch
DSV : Distillats Sous Vide
EIC : Chromatogramme obtenu en suivi d'ions (Extracted Ion Chromatogram)
EOR : Enhanced Oil Recovery
ESI : Ionisation électrospray (ElectroSpray Ioniztion)
ETAAS : Spectroscopie d’absorption atomique électrothermique (ElectroThermal Atomic Absorption Spectroscopy)
ETV : Vaporisation électrothermique (Electrothermal Vaporization)
FCC : Fluide de craquage catalytique (Fluid Catalytic Cracking)
FID : Détecteur à ionisation de flamme (Flame Ionization Detector)
FS : Full Scan
FT-ICR/MS : Spectrométrie de masse à résonance cyclotronique ionique et à transformée de Fourier (Fourier Transform Ionization Cyclotron Resonance Mass Spectrometry)
FTIR : Spectroscopie infra rouge à transformée de Fourier (Fourier Transform Infra Red Spectroscopy)
FT/MS : Spectrométrie de masse à transformée de Fourier (Fourier Transform Mass Spectrometry)
GC : Chromatographie en phase gazeuse (Gas Chromatography)
GC-GC : Chromatographie en phase gazeuse "coupe de cœur" (heart cutting Gas Chromatography)

GCxGC : Chromatographie en phase gazeuse bidimensionnelle (Comprehensive Gas Chromatography)
GFAAS : Absorption atomique par four graphite (Graphite Furnace Atomic Absorption Spectroscopy)
GPL : Gaz de Pétrole Liquéfié
HCK : Hydrocraquage (HydroCracKage)
HDPE : Polyethylène haute densité (High Density PolyEthylene)
HDT : Hydrotraitement (HyDroTreatment)
HDN : Hydrodénitrification (HydroDeNitrification)
HDS : Hydrodésulfuration (HyDrodeSulfuration)
HMW : Haut poids moléculaire (High Molecular Weight)
HPLC : Chromatographie liquide haute performance (High Performance Liquid Chromatography)
HPV : Haut volume de production (High Production Volume)
HR : Haute résolution (High Resolution)
HS : Espace de tête (Head Space)
HT : Haute température (High Temperature)
HYD : Hydrogénation (HYDrogenation)
IC : Ionisation chimique (Chemical Ionization)
IE : Ionisation par impact électronique (Electron Ionization)
ICP : Plasma à Couplage inductif (Inductively Coupled Plasma)
ICP/MS : Spectrométrie de masse par plasma à couplage inductif (Inductively Coupled Plasma Mass Spectrometry)
ICP-OES : Spectrométrie d’émission optique par plasma à Couplage Inductif (Inductively Coupled Plasma Optic Emission Spectroscopy)
IR : Spectroscopie infra-rouge (Infra Red spectroscopy)
IUPAC : International Union of Pure and Applied Chemistry
KMD : Défaut de masse de Kendrick (Kendrick Mass Defect)
LA : Ablation laser (Laser Ablation)
LOQ : Limite de quantification (Limits Of Quantification)
LC : Chromatographie en phase liquide (Liquid Chromatography)
LCO : Gazole léger de craquage catalytique (Light Cycle Oil)
LMW : Bas poids moléculaire (Low Molecular Weight)
LOD : Limite de détection (Limit Of Detection)

LT : Basse température (Low Temperature)

MALDI : Ionisation/désorption laser assistée par une matrice (Matrix Assisted Laser Desorption Ionization)

MC : Multi-collecteur (Multi Collector)

MPT-OES : Spectroscopie d'émission optique par torche à plasma micronde (Microwave Plasma Torch Optical Emission Spectroscopy)

MM : Masse moléculaire (Molecular Mass)

MS : Spectrométrie de masse (Mass Spectrometry)

MS/MS : Spectrométrie de masse en tandem (Tandem Mass Spectrometry)

NASA : National Aeronautics and Space Administration

NIST : National Institute of Standards and Technology

NMR : Résonance magnétique nucléaire (Nuclear Magnetic Resonance)

NP : Phase normale (Normal Phase)

NSO : Azotés, soufrés et oxygénés (Nitrogen, Sulfur, Oxygen)

OECD : Organisation for Economic Co-operation and Development

PDMS : Polydiméthylsiloxane (Polydimethylsiloxanes)

PTFE : Téflon (Teflon)

QMS : Quadrupole Mass Spectrometry

RA : Résidu Atmosphérique

RF : Facteur de réponse (Response Factor)

RI : Indice de réfraction (Refractive Index)

RSD : Déviation standard (Relative Standard Deviation)

RSV : Résidu Sous Vide

RON : Indice d'octane recherche (Research Octane Number)

RP : Phase inverse (Reverse Phase)

SEC : Chromatographie d’exclusion stérique (Size Exclusion Chromatography)

SFC : Chromatographie en phase supercritique (Supercritical Fluid Chromatography)

Si : Silicium (Silicon)

SIM : Selected Ion Monitoring

TIC : Courant ionique total (Total Ion Current)

TISIS : Système d’introduction totale de l’échantillon (Total Integrated Sample Introduction System)

TOF : Analyseur de masse à temps de vol (Time of Flight)

USEPA : US Environmental Protection Agency

USN : Nébuliseur ultrasonique (Ultrasonic Nebulizer)

UV : Ultra-violet

VMS : Volatile MethylSiloxanes

VOC : Composé organique volatil (Volatile Organic Compound)

XRF : Fluorescence par rayons X (X-Rays Fluorescence)

Résumé

Le silicium est connu pour être un poison sévère des catalyseurs d'hydrotraitement (HDT), notamment au niveau des coupes essences. Cependant, les molécules silicées pouvant être en contact avec les phases actives des catalyseurs sont inconnues et présentes à l'état de traces (µg.kg^{-1}). Elles proviennent de la dégradation thermique des agents anti-mousse de type polydiméthylsiloxanes (PDMS) ajoutés dans les charges pétrolières. L'objectif de la thèse est de mettre en place des outils analytiques pour la spéciation du silicium afin d'identifier toutes les molécules silicées réellement formées dans les charges d'HDT et potentiellement poisons des catalyseurs.

Afin de construire notre stratégie analytique, différents outils analytiques de pointe ont été développés dans des essences réelles. La GC/MS SIM permet une analyse qualitative et quantitative des composés silicés connus à l'état de traces. Néanmoins, pour la caractérisation des composés silicés inconnus, une nouvelle méthode par ESI-FT-ICR/MS associée à la construction de diagrammes de Kendrick a été mise en place. L'accès à la structure chimique de ces espèces est freiné par le nombre d'isomères possibles. Pour ce faire, l'association entre les temps de rétention obtenus par GC-ICP/MS et les spectres de masse fournis par GC-GC/TOFMS a été effectuée.

Étant donnée la réactivité de certaines espèces silicées, des échantillons représentatifs de la dégradation du PDMS ont été produits dans des conditions de craquage thermique d'un mélange heptane/xylène. L'application à ces échantillons de la stratégie analytique, développée initialement, démontre la présence du silicium sous différentes formes chimiques. Plus d'une centaine de molécules réparties en 10 familles comprenant un nombre d'atomes de silicium entre 1 et 1500 a été caractérisée qualitativement. Ces composés silicés vont donc pouvoir être présents dans toutes les coupes pétrolières, des fractions gaz aux fractions les plus lourdes, couvrant ainsi un domaine de coupes pétrolières beaucoup plus vaste que celui des naphtas et des essences. Les siloxanes cycliques (D_n) ont été confirmés comme produits majoritaires de dégradation du PDMS (environ 95%). Les autres composés silicés, jamais caractérisés pour la plupart, sont présents à l'état de traces (environ 5%) mais possèdent des groupements réactifs de type hydroxy, métoxy, hydropéroxy susceptibles d'interagir fortement avec le support du catalyseur (Al_2O_3) et de conduire à sa désactivation. Contrairement aux D_n, la formation de ces espèces silicées est dépendante des conditions appliquées dans les procédés de raffinage.

Jusqu'à présent, des tests d'empoisonnement avaient été effectués sur des molécules modèles choisies sans connaître les véritables composés présents dans les charges et les résultats n'étaient pas toujours concordants. Grâce à la stratégie multi-technique inédite basée sur des outils analytiques de pointe, la caractérisation d'une multitude d'espèces silicées dans des échantillons représentatifs démontre la présence du silicium dans toutes les coupes pétrolières. Ces résultats ouvrent donc de nouvelles perspectives pour progresser sur la compréhension de l'empoisonnement par le silicium.

Abstract

Silicon is known to be a severe poison for hydrotreatment (HDT) catalysts especially in naphtha and gasoline samples. However, silicon compounds present in petroleum products and potentially affecting the active catalytic phases were unknown and present at trace levels (µg.kg^{-1}). Silicon species mainly originate from the thermal degradation of antifoaming agents such as polydimethylsiloxanes (PDMS) added in feeds to avoid emulsions. The objective of the PhD is to develop analytical methods for silicon speciation in order to characterize silicon molecules formed during refining steps which potentially affects HDT catalysts.

For the analytical strategy, different high-technology analytical tools were developed in real gasoline samples. GC/MS SIM provided sufficient sensitivity and selectivity for the analysis of known silicon compounds at trace levels in gasoline. For the characterization of unknown silicon compounds, a novel approach involving ESI-FT-ICR/MS and Kendrick plots data processing was implemented. However, the chemical struture cannot be obtained because of the number of possible isomers. To give access to the structural elucidation of the species, a complementary approach between GC-ICP/MS and GC-GC/TOFMS was developed.

Due to the high reactivities of several silicon species, representative samples of PDMS degradation were produced under thermal cracking of a mixture of heptane/xylene (500°C) using a pilot plant. The previously developped analytical strategy was applied to these samples and demonstrated the occurrence of silicon under a wide array of chemical forms. More than a hundred of silicon species belonging to 10 chemical families with a number of silicon atoms ranging from 1 to 1,500 were characterized. These silicon compounds could be present in all petroleum cuts, from the gas fractions to the heavier fractions. Therefore, the investigated range of boiling points was inevitably more important than for naptha and gasoline cuts. Cyclic siloxanes (D_n) were confirmed as the major PDMS degradation products (around 95%). The other silicon compounds, almost never characterized before, were recovered at trace levels (around 5%) but consisted of reactive groups such as hydroxy, methoxy and hydroperoxy. These silicon species were able to strongly react with the catalytic support (Al_2O_3) and led to its deactivation. Contrary to D_n, the formation of these silicon species was dependent on the applied conditions to refining process (time residence, temperature, steam content).

Up to now, poisoning tests have been carried out using model molecules without knowing the exact nature of silicon species really present in petroleum products. Results did not allow to conclude about the poisoning effect. Thanks to the multi-technical analytical strategy based on high-technology analytical systems, the characterization of a wide array of species in representative samples demonstrates the presence of silicon in all petroleum cuts. Thus, these results brought novel prospects to progress on the understanding of silicon poisoning.

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Introduction

Depuis plusieurs années, l'industrie pétrolière doit faire face d'une part à une demande en produits légers et intermédiaires (GPL, essence, kérosène, gazole) de plus en plus forte et d'autre part à une diminution des ressources avec des pétroles de plus en plus lourds et de moins en moins bonne qualité (composés NSO et métaux en quantité plus importante) [1]. Ces différentes contraintes conjuguées à la sévérisation des spécifications environnementales entraînent un besoin constant d'amélioration des procédés de raffinage et des techniques analytiques notamment pour déterminer la présence d'impuretés à l'état de traces. Malgré le développement de nouveaux catalyseurs toujours plus performants, la formation de coke, le frittage de la phase métallique et **la contamination par différents éléments chimiques**, restent les trois phénomènes de désactivation des catalyseurs [2]. Ils contribuent à diminuer considérablement la durée de vie de ces systèmes. Les deux premiers phénomènes sont atténués après régénération du catalyseur (oxydation du catalyseur à haute température). Au contraire, la présence de différents éléments chimiques (Si, V, Ni, As, Pb, Hg, Al) retrouvés à la surface du catalyseur subsiste et entraîne **un phénomène de désactivation** souvent irréversible. Ce phénomène dépend de la quantité de poisons retrouvée dans les charges pétrolières mais également de leur nocivité. L'empoisonnement conduit généralement au remplacement prématuré du catalyseur et donc à une perte économique non négligeable.

Le **silicium (Si)** est particulièrement connu pour être **un poison sévère des catalyseurs d'hydrotraitement (HDT)** [3, 4]. Lorsque que la concentration en silicium atteint quelques mg de Si.kg^{-1}, la durée typique d'un cycle d'HDT d'un naphta, généralement de 3 ans, est réduite à 12 mois voire 6 mois et moins dans des cas extrêmes [4]. Afin d'assurer le maintien de l'activité du catalyseur, il est nécessaire de pouvoir caractériser le silicium dans les charges pétrolières. L'origine du silicium dans les charges pétrolières provient majoritairement de **l'ajout d'agents antimousse de type polydiméthylsiloxanes (PDMS)** à des concentrations de l'ordre de 1 à 20 mg.kg^{-1} afin d'éviter les émulsions dans les différents procédés [5-7]. Malgré une grande stabilité thermique jusqu'à 300°C [8-13], le PDMS va se dégrader à cause des températures appliquées qui sont généralement comprises entre 300 et 800°C selon les différentes étapes du raffinage. La formation d'une multiplicité de **composés silicés à l'état de traces** va donc être observée. Ces espèces vont ensuite pouvoir affecter les performances des systèmes catalytiques [14]. La dégradation thermique du PDMS sous atmosphère interne a largement été étudiée dans la littérature [8-13] mais jamais dans des conditions de raffinage des produits pétroliers. Les **molécules silicées formées** dans les produits pétroliers sont donc

peu connues à ce jour. Seul un **dosage total du silicium** est effectué par spectroscopie d'émission optique par plasma à couplage inductif (ICP-OES) ou par spectrométrie de masse par plasma à couplage inductif (ICP/MS) [15, 16]. Les concentrations généralement reportées sont comprises entre **quelques centaines de µg de Si.kg^{-1} et quelques mg de Si.kg^{-1}** [17, 18]. Afin de comprendre l'empoisonnement des catalyseurs et limiter ce phénomène, l'accès à la concentration totale en silicium est insuffisant. La réalisation d'une **spéciation de ce poison à l'état de traces dans les différentes charges d'hydrotraitement** est donc nécessaire. Ce besoin s'avère crucial notamment au niveau des **coupes naphtas et essences** où le silicium est majoritairement quantifié aux teneurs les plus importantes et pose donc les problèmes d'empoisonnement les plus conséquents.

Selon l'IUPAC [19], la **spéciation d'un élément** est définie par la **distribution de ses différentes formes chimiques** dans un échantillon. Plus précisément, une analyse de spéciation peut être considérée comme **l'identification et la quantification** des différentes formes physiques et chimiques d'un élément dans un analyte [20]. Pour ce faire, des techniques de couplage entre des techniques séparatives et une détection sensible et sélective semblent être les outils les plus adaptés [19, 21]. Le faible nombre de travaux reportés pour la spéciation du silicium, notamment dans le domaine pétrolier où aucune étude n'a été reportée, suscite donc un véritable défi analytique [14].

L'objectif de mon travail de thèse a consisté à **mettre en place un ou plusieurs outils de spéciation du silicium** afin de **déterminer les molécules silicées formées dans les charges d'hydrotraitement**. La caractérisation des différentes formes chimiques du silicium dans les produits pétroliers doit permettre de développer de futures solutions technologiques innovantes et respectueuses de l’environnement pour limiter l’empoisonnement des catalyseurs par le silicium et donc améliorer considérablement leur durée de vie actuelle.

Ce manuscrit est divisé en quatre parties et est composé de huit chapitres. Il s'appuie majoritairement sur plusieurs publications parues, à paraître, en cours d'évaluation ou de préparation dans des journaux scientifiques dans le domaine de la chimie analytique et dans le domaine pétrolier.

La **Partie A** présente l'étude bibliographique de manière à identifier les principaux verrous à lever pour atteindre l'objectif de mon travail. Cette partie aborde d'une part l'origine et l'impact du silicium dans l'industrie pétrolière et d'autre part les différentes techniques analytiques utilisées pour l'analyse du silicium total mais surtout pour les études de spéciation. Une attention toute particulière sera portée à la réactivité de certains composés silicés et aux potentiels problèmes de contamination rencontrés lors de l'analyse du silicium.

La **Partie B** présente le développement de différents outils analytiques de pointe afin de construire une solution analytique adaptée pour réaliser une spéciation du silicium dans des échantillons réels de naphtas et d'essences. Dans un premier temps, la GC/MS en mode single ion monitoring (SIM) a été mise en œuvre pour l'identification et la quantification de molécules silicées disponibles commercialement. Dans un deuxième temps, des travaux par spectrométrie de masse haute résolution (FT-ICR/MS) combinés à la construction de diagrammes de Kendrick ont été effectués pour parvenir à une information qualitative plus étendue des molécules silicées par leur formule brute et leur nombre d'insaturations. Néanmoins, l'accès à la structure chimique reste limité par le nombre d'isomères possibles. Pour ce faire, une approche inédite a été menée entre la GC-ICP/MS permettant une détection spécifique des temps de rétention des composés silicés et la GC-GC/TOFMS donnant accès à leur spectre de masse et donc à une orientation vers leur structure chimique.

Après avoir construit notre stratégie multi-technique inédite autour des différents outils analytiques, la **Partie C** présente la spéciation du silicium effectuée dans des échantillons représentatifs. Pour ce faire, des échantillons "frais" de dégradation du PDMS dans un mélange de solvants modèles et sous des conditions de craquage thermique ont été produits sur une unité pilote. Le but est de déterminer la structure chimique des composés silicés réellement retrouvés au moment de l'empoisonnement dans les coupes naphtas et essences mais également au sein des autres coupes pétrolières, potentiellement concernées par la présence du silicium.

Pour finir, la **Partie D** de ce manuscrit illustre l'apport de la spéciation du silicium pour l'industrie pétrolière. Grâce à la description complète de la stratégie analytique inédite mise en place lors de mon travail de thèse, les différentes molécules silicées caractérisées sont présentées par famille et selon leurs conditions de formation. Certaines hypothèses concernant la potentielle réactivité des composés silicés dans les produits et vis à vis des phases catalytiques sont également abordées.

Partie A. Étude bibliographique

Chapitre 1. Raffinage et produits pétroliers : Origine et impact du silicium

1.1 Introduction

Le raffinage est défini par l'ensemble des opérations mises en œuvre pour transformer le pétrole brut en carburants (GPL, essences, gazoles), combustibles (gaz, fiouls) et produits spéciaux pour la pétrochimie (éthylène, butadiène) [22]. Chacun de ces produits doit répondre à des spécifications précises qui sont révisées périodiquement. Pour ce faire, de nombreux traitements et transformations du pétrole brut sont réalisés dans un ensemble d'unités faisant appel à plusieurs familles de procédés. La Figure 1-1 distingue les trois grandes étapes du raffinage et précise schématiquement l’ajout de PDMS dans ces différents procédés. Après un dessalage pour éliminer les minéraux, le premier traitement consiste à effectuer une distillation du brut (atmosphérique puis sous vide) afin d'obtenir plusieurs coupes pétrolières. Ces coupes vont ensuite être dirigées vers des procédés de transformation, composés d'unités d'amélioration des propriétés (reformage, isomérisation...) et de conversion (viscoréduction, cokéfaction, vapocraquage...) qui génèrent de nouvelles molécules plus adaptées à l'usage du produit. Des procédés de finition (hydrotraitement : HDT) vont également être mis en œuvre lors du raffinage pour éliminer les composés indésirables. A la suite de cette étape, des bases sont ainsi obtenues puis mélangées pour obtenir les produits finis de qualité (GPL, essence, gazole...) tout en respectant la protection de l'environnement.

Étant donné le nombre important de procédés, cette partie ne sera pas exhaustive et se focalisera principalement sur les procédés dans lesquels le PDMS est ajouté et sur les procédés d'hydrotraitement (HDT) qui sont fortement impactés par la présence de silicium. A cette étape, il nous paraît nécessaire de faire un bref rappel des différents constituants des pétroles bruts.

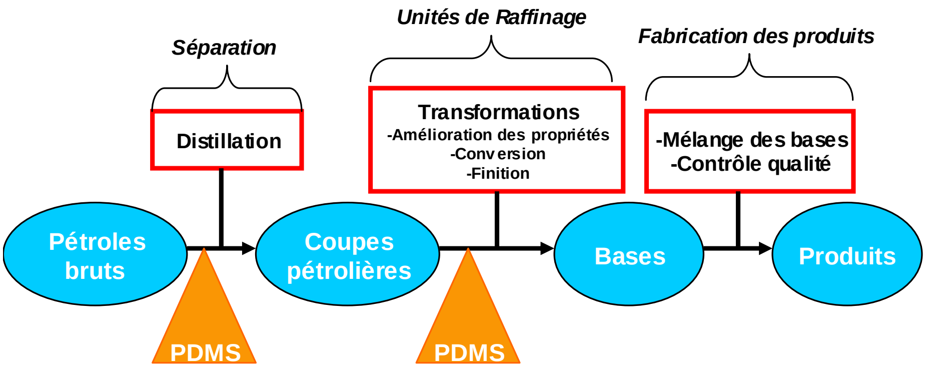


Figure 1-1. Différentes étapes du raffinage [1]

1.2 Composition des pétroles bruts

Le pétrole brut est un mélange complexe d'hydrocarbures (molécules formées de carbone et d'hydrogène) associés à des composés hétéroatomiques ainsi qu'à des traces de métaux et d'impuretés. Ce mélange contient des millions de molécules différentes qu'il va falloir fractionner et transformer chimiquement pour obtenir des produits utilisables. Il s'agit d'une des matrices les plus complexes à caractériser d'un point de vue analytique [23].

Le pétrole possède des propriétés physiques et chimiques très variables d'un champ de production à un autre, mais également à l'intérieur du gisement [24]. Une première différenciation est faite entre les pétroles lourds et légers. Étant constitués majoritairement de molécules hydrocarbonées (carbone et hydrogène), la densité d'un pétrole sera d'autant plus faible que son rapport atomique hydrogène/carbone est élevé. Cette valeur oscille généralement entre 0,7 et 1 pour les pétroles bruts. Plusieurs hétéroatomes (soufre, azote, oxygène) (Annexe 1) et certains métaux (fer, nickel, vanadium), principalement contenus dans les coupes lourdes (asphaltènes et résines) sont également présents. Le Tableau 1-1 présente la proportion globale des différents constituants du pétrole en pourcentage massique. Ces familles seront brièvement décrites par la suite.

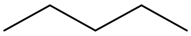
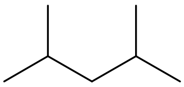
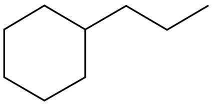
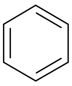
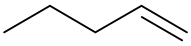
Tableau 1-1. Composition globale des pétroles bruts [24]

Familles	Constituants	% en masse
Hydrocarbures	Carbone (C)	84 à 87
	Hydrogène (H)	11 à 14
Composés organiques hétéroatomiques	Soufre (S)	0,04 à 6
	Oxygène (O)	0,1 à 0,5
	Azote (N)	0,1 à 1,5
Composés Organométalliques	Métaux	0,005 à 0,015
Autres	Eau et sédiments	0,1 à 0,6
	Sels minéraux	0,002 à 0,02

1.2.1 Hydrocarbures

Les hydrocarbures sont les principaux constituants des pétroles. Ils ne contiennent que du carbone et de l'hydrogène et se divisent en plusieurs familles chimiques. Un bref rappel de ces différentes familles est effectué dans le Tableau 1-2. Nous distinguons deux principaux groupes, les hydrocarbures saturés (paraffines, naphtènes) et les hydrocarbures insaturés (aromatiques, oléfines). La première famille ne contient pas de liaisons multiples ou de cycles aromatiques, toutes les liaisons sont saturées par l'hydrogène (C-H).

Tableau 1-2. Différentes familles d'hydrocarbures et quelques exemples

Hydrocarbures Saturés			Hydrocarbures Insaturés	
Hydrocarbures présents dans les pétroles bruts				Produits lors des traitements
Paraffines		Naphtènes	Aromatiques	Oléfines
Paraffines Normales	Isoparaffines	Cycloparaffines		
Chaîne linéaire	Chaîne ramifiée	Cycles	Cycles benzéniques	Chaîne avec double liaison
C_nH_{2n+2}		C_nH_{2n}	C_nH_{2n-6k} C_nH_{2n-8k}	C_nH_{2n}
 Pentane	 1,4-Dimethylpentane	 Propylcyclopentane	 Benzène	 1-Pentène

Avec n le nombre de Carbone et k le nombre de cycles

Suite à la distillation atmosphérique du pétrole brute (Figure 1-1), les hydrocarbures et autres composés vont être présents dans les différentes coupes pétrolières en fonction de leur point d'ébullition et donc de leur nombre de carbone (n). Ainsi, sont obtenues un mélange de gaz en tête de colonne, puis par ordre croissant d'ébullition : naphta/essence, kérozène, gazole et résidu atmosphérique (RA) (Figure 1-3). Le Tableau 1-3 présente le nombre de carbone et les différents intervalles de points d'ébullition de ces coupes pétrolières. Dans ce travail de thèse, nous nous focaliserons principalement sur les coupes naphta et essences (C_5-C_{10}) dans lesquelles le silicium est majoritairement retrouvé et va engendrer des problèmes d'empoisonnement au niveau des procédés de finition (HDT). L'appellation "naphta" est plutôt réservée aux coupes pétrolières qui vont servir de produits de base à la pétrochimie (vapocraquage). Le terme "essence" correspond aux coupes qui vont être transformées en carburants. Néanmoins, il est intéressant de décrire brièvement les coupes les plus lourdes contenant de nombreux poisons pour les catalyseurs (S, N, Ni, V).

Tableau 1-3. Exemple du nombre de carbones et des points d'ébullition des différentes coupes pétrolières [1, 24]

Coupes pétrolières	Gaz	Naphta/Essence	Kérozène	Gazole	Distillat sous vide	Résidu sous vide
Nombre d'atomes de carbone	C_1-C_4	C_5-C_{10}	C_6-C_{16}	C_{11}-C_{20}	C_{20}-C_{50}^+	$>C_{50}$
Intervalle des points d'ébullition (°C)	-100/20	20/180	120/280	180/350	350/600	600^+

Le résidu atmosphérique peut ensuite être séparé par une distillation sous vide, en deux autres coupes pétrolières : les distillats sous vide (DSV) et les résidus sous vide (RSV). Cette opération est effectuée sous vide afin d'éviter le craquage des liaisons atomiques qui se produit au delà de 400°C (Figure 1-3 et Annexe 2). Ces fractions pétrolières lourdes sont des coupes de haut point d'ébullition (>350°C). Elles comprennent donc les coupes RA, DSV et RSV. Elles sont composées des molécules de plus hautes masses moléculaires et les plus polaires tels que les asphaltènes et les résines. Etant donnée la polydispersité de ces dernières fractions, leurs propriétés structurelles et chimiques ne peuvent être déterminées que moyennées et elles ne sont définies que par leurs conditions opératoires d'obtention.

Les asphaltènes, sont généralement considérés comme la fraction d'une huile brute qui précipite avec un fort excès d'un alcane pouvant être selon les normes le pentane, l'hexane et l'heptane mais solubles dans le toluène [25]. Ils sont constitués d'une accumulation de feuillets polyaromatiques condensés reliés par des chaînes saturées et leur masse moléculaire peut varier de 1000 à 100000 $g.mol^{-1}$ suivant la méthode d'analyse utilisée et leur état d'agrégation.

La partie soluble dans le solvant paraffinique est constituée par les maltènes. Si l'on soumet, cette fraction à une chromatographie liquide, les produits élués avec les solvants les plus polaires sont appelés résines [24]. Il s'agit généralement de molécules à caractère aromatique très marqué avec des masses moléculaires comprises entre 500 et 1000 $g.mol^{-1}$. Les résines jouent un rôle essentiel dans la stabilité du pétrole en prévenant la démixtion des asphaltènes.

Il est important de souligner que ces molécules contiennent de nombreuses impuretés (S, O, N, V, Ni) et restent concentrées dans les coupes pétrolières les plus lourdes, non distillables. Elles constituent un obstacle aux opérations de conversion des produits pétroliers.

1.2.2 Composés organiques hétéroatomiques

Le soufre est l'hétéroélément le plus abondant dans les pétroles bruts. Sa concentration peut aller de 0,04 à 6 % en masse. Il peut être présent sous 4 formes principales associées au carbone et à l'hydrogène (H_2S, mercaptans, sulfures et thiophènes). L'élimination et la caractérisation de ces composés [26] sont nécessaires dans les procédés de raffinage (HDS) car ils sont à l'origine des empoisonnements des catalyseurs (procédés de raffinage ou pots catalytiques) mais également des pollutions atmosphériques. De plus, les normes concernant la quantité en soufre des produits pétroliers (<10 ppm [2]) sont de plus en plus contraignantes.

D'une manière générale, l'azote se retrouve sous plusieurs formes chimiques mais à des concentrations bien inférieures (0,1 à 1,5 % en masse) à celles du soufre. Il se trouve principalement dans des coupes lourdes (>250 °C) et est particulièrement concentré dans les asphaltènes et les résines. Ces molécules peuvent être classées en deux familles : les composés neutres (carbazoles) où un cycle azoté peut être condensé à un ou plusieurs cycles aromatiques et les composés basiques (pyridines) [27]. Le caractère basique très marqué de certains d'entre eux entraîne un obstacle à la conversion des coupes lourdes et un empoisonnement des catalyseurs acides.

Bien que peu présents dans les pétroles (0,1 à 0,5 % en masse), les composés oxygénés confèrent un caractère acide au pétrole et entraînent donc des problèmes de corrosion. Ils se retrouvent également dans les coupes issues de la biomasse. Ces composés peuvent apparaître sous plusieurs formes chimiques (phénols, naphtols, furanes, benzofuranes, acides carboxyliques et esters) [28]. Une représentation de différents composés NSO (azotés, soufrés et oxygénés) présents dans les produits pétroliers est donnée en Annexe 1.

1.2.3 Composés Organométalliques

Les métaux (essentiellement Ni et V) se situent dans les coupes lourdes (asphaltènes et résines) précédemment décrites et sont notamment connus pour empoisonner les catalyseurs d’hydrotraitement (HDT). Ils forment des complexes avec des molécules porphyriniques (Figure 1-2) où le motif de base est constitué par quatre cycles pyrroliques qui entourent le métal (Ni^{++}, VO^{+}). De récents travaux au sein d'IFPEN sur la caractérisation de ces composés dans les fractions lourdes du pétrole ont été effectués par Caumette *et al.* [29].

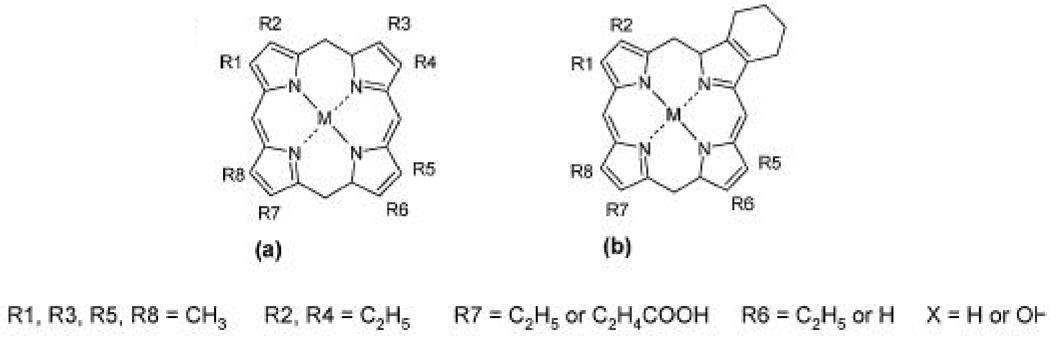


Figure 1-2. Structure de deux porphyrines (M=Ni ou V) retrouvées dans les produits pétroliers : a-étio porphyrine et b-tétrahydrobenzoporphyrine [29]

D'autres impuretés (As, Hg, Na, Fe, Pb, Cl, et Si) sont également présentes dans les produits pétroliers en très faibles quantités mais vont avoir tendance à empoisonner les catalyseurs d'HDT et donc réduire leur durée de vie [2]. Le Tableau 1-4 rappelle ces différents éléments ainsi que leur origine, leurs effets sur le catalyseur et la teneur maximale supportée par ce dernier. Ces composés se trouvent à l'état de traces dans la majorité des produits pétroliers et proviennent de diverses origines. Comme le Ni et le V, l’As, le Hg et le Na sont naturellement présents dans les charges. A l’inverse, le silicium est issu d’additifs lors des opérations de raffinage, d'extraction assistée ou comme le Fe, produit par corrosion [2]. A la vue du Tableau 1-4, Il est vrai que le silicium pose des problèmes moins importants que l'As ou le Ni et V. Néanmoins, l'ajout d'agents antimousse dans de nombreux procédés de raffinage et lors de l'extraction assistée du pétrole brut (Enhanced Oil Recovery, EOR) augmente la concentration en silicium dans les charges d'HDT et va conduire à des empoisonnements plus sévères.

Tableau 1-4. Différents poisons des catalyseurs [24]

Impuretés	Source	Coupe principale	Empoisonnement du catalyseur	Teneur maximale sur le catalyseur (% masse)
Ni, V	Brut	Distillats Résidus	Fort, dépôt à l'intérieur du catalyseur et bouchage	10 30-40
As	Brut	Toutes	Fort, dépôt en tête de réacteur	0,2-2
Hg	Brut	Naphta	Faible, impureté peu retenue	traces
NaCl	Brut	Résidus	Fort, dépôt en tête de réacteur, génère une perte de charge	1,0
Fe	Brut et corrosion	Toutes	Faible, dépôt en tête de réacteur, génère une perte de charge	1
Cl	Solvants, sloop recyclés		Très faible, dépôt à l'intérieur du catalyseur et bouchage	0,1-0,5
Pb	Essence recyclée	Essence	Fort, dépôt en tête de lit	0,1-1,5
CO/CO_2	Appoint d'hydrogène	Toutes	Très faible, formation de Ni, Co, Fe carbonyle à basse température	<0,05 %vol
Si	Antimousse	Distillats	Très faible, dépôt à l'intérieur du catalyseur et bouchage	5-10

1.3 Origine du silicium dans les produits pétroliers

1.3.1 Antimousse et Conséquences

Les conditions appliquées (température, différence de pression) et les processus mis en œuvre dans les procédés pétroliers (agitation, distillation) utilisés lors du raffinage du pétrole brut conduisent à la formation d'émulsions [6]. En effet, la génération de vapeurs et la présence de surfactants naturels (asphaltènes et résines) sont les principales causes de formation de mousses dans les procédés de cokéfaction [6, 30]. La présence de mousses peut causer de nombreux problèmes d'efficacité et de maintenance. Dans le but d'éviter l'apparition de ces phénomènes, des agents antimousse à base de silicium, plus généralement appelés silicones sont ajoutés dans les charges en raison de leurs propriétés de surface et de leur relative stabilité thermique. Le polydiméthysiloxane (PDMS) est l'antimousse le plus utilisé dans l'industrie pétrolière dû à son large domaine d'applications [5-7]. Il existe néanmoins d'autres agents antimousse mais toujours à base de silicium tels que les fluorosilicones et les silicones glycols [7]. Par exemple, les fluorosilicones vont être employés lors de problèmes avec des environnements agressifs tels que le traitement de pétrole contenant d'importantes concentrations en soufre (>0,5% en masse) mais ils seront moins efficaces que le PDMS pour des applications plus classiques [7].

Le polydiméthylsiloxane (PDMS) est principalement ajouté pour la récupération du brut, le dessalage, l'extraction des asphaltènes et le transport dans les pipelines mais également lors du traitement des acétyléniques et dans différentes unités telles que les colonnes de distillation atmosphériques, les procédés de conversion thermique (cokéfaction, viscoréduction et vapocraquage) et le désalphatage du propane [5, 6, 30-32].

La Figure 1-3 présente une succession de procédés pétroliers généralement retrouvés dans les raffineries suite à la distillation du pétrole brut. Les catalyseurs présents, notamment au niveau des procédés d'hydrotraitement (HDT) peuvent être impactés par le silicium tout au long de la chaîne du raffinage. La quantité de PDMS, injectée en début de procédé de raffinage, généralement d'une viscosité de 60,000 cSt, varie en fonction de la quantité de charges à démousser et du procédé en question. Par exemple, lors d'un procédé de cokéfaction retardée (temps de séjour plus long) ou lors d'un ajout pour limiter le moussage lors d'une séparation gaz/huile, la quantité de PDMS oscille entre 1 et 20 $mg.kg^{-1}$ [5] mais peut atteindre des teneurs de 50 $mg.kg^{-1}$ à quelques centaines de $mg.kg^{-1}$ dans des cas extrêmes [33].

La température élevée au sein des procédés de raffinage entraîne néanmoins une dégradation du polymère malgré une stabilité thermique importante de ce dernier (300°C) [8-10, 12, 13, 34]. Cette dégradation conduit majoritairement à la formation de siloxanes cycliques (D_n) mais également à la possible production d'une multiplicité de composés silicés peu connus, dépendante des conditions de dégradation (oxygène, rampe de température, impuretés, hydrocarbures) (Figure 1-3). De plus amples détails sur ces travaux de dégradation du PDMS sont donnés dans la section 2.2.2. Dans les conditions sévères appliquées dans l'industrie pétrolière, les produits de dégradation du PDMS et de réaction avec la matrice pétrolière sont totalement inconnus.

1.3.2 Procédés pétroliers impactés par le silicium

Le but de cette partie est de décrire de façon synthétique les différents procédés pétroliers pour lesquels le silicium est présent et peut ensuite poser des problèmes dans les procédés d'hydrotraitement. La connaissance de ces procédés permettra de mieux représenter les conditions de dégradation du PDMS pour la production des échantillons afin d'obtenir une spéciation représentative. Ce travail sera développé dans la partie C de ce mémoire.

La Figure 1-3 présente les différents procédés de raffinage suite à l'étape de distillation du pétrole. Comme nous l'avons mentionné précédemment, l'ajout de PDMS va conduire à la formation de diverses molécules silicées sous différentes formes chimiques pour le moment inconnues. Elles vont ensuite distiller dans les différentes coupes pétrolières et potentiellement affecter les catalyseurs utilisés dans les procédés d'hydrotraitement (HDT) (Figure 1-3). Les points d'ébullition des différentes coupes pétrolières ainsi que le nombre de carbone (Tableau 1-3) présent sont rappelés sur cette figure. Les procédés qui vont être décrits sont ceux pour lesquels le PDMS est connu pour être ajouté en tant qu'agent antimousse. Néanmoins, une synthèse des différents procédés de raffinage est donnée en Annexe 2 accompagnée de leurs conditions respectives en Annexe 3.

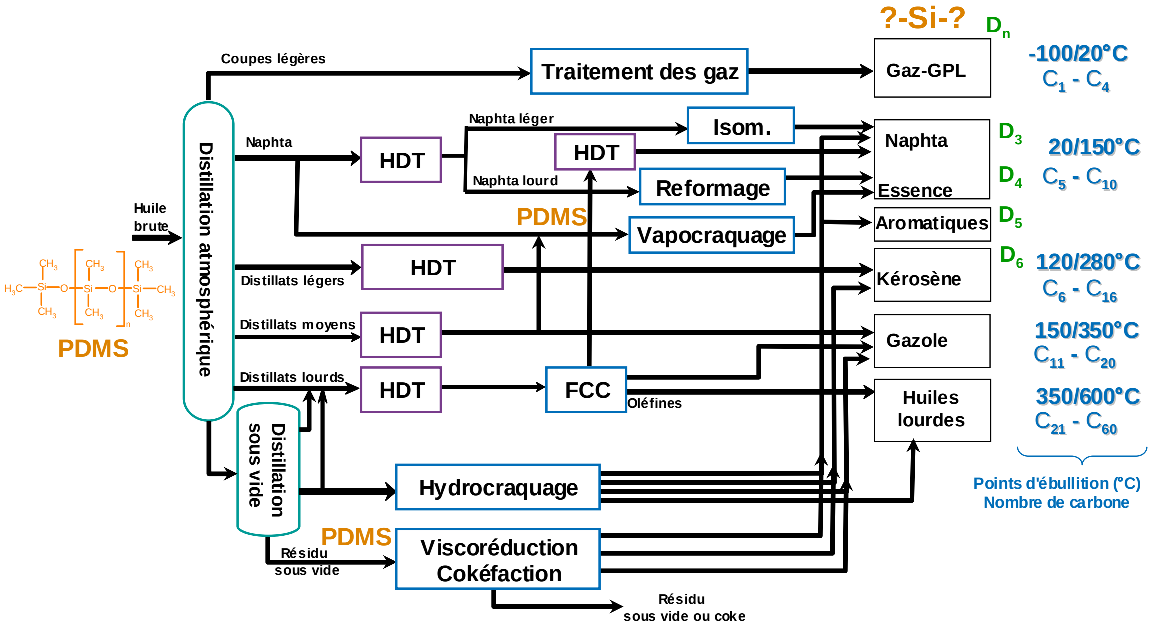


Figure 1-3. Schéma des différents procédés pétroliers précisant l'ajout d'agents antimousse

HDT : Hydrotraitement ; FCC : Fluid Catalytic Cracking ; Isom. : Isomérisation ; GPL : gaz de pétrole liquéfié

1.3.2.1 Distillation atmosphérique

Généralement, le PDMS n'est pas ajouté lors de l'étape de distillation du pétrole brute. Au contriare, il peut être ajouté dès l'étape d'extraction du pétrole brut afin d'améliorer les rendements d'extraction (EOR) ou avant l'étape de distillation atmosphérique pour éviter les émulsions [5, 6]. Étant donnée la température appliquée au sein de la colonne de distillation (jusqu'à 350°C), le PDMS peut commencer à se dégrader et former des produits silicés de plus basse massesmoléculaire. Suite à cette étape (Figure 1-3), plusieurs coupes pétrolières (légères, naphta, distillats et résidus atmosphériques) vont être obtenues puis dirigées vers différents procédés de raffinage afin d'être transformées en produits commerciaux finis (GPL, essence, kérosène, gazole, huiles).

1.3.2.2 Procédés de conversion

1.3.2.2.1 Cokéfaction et Viscoréduction

La viscoréduction [35] et la cokéfaction [36] sont les deux principaux procédés utilisés pour la conversion des produits lourds. Ces procédés ont pour but de craquer thermiquement à 500°C les résidus atmosphériques ou sous vide afin d'obtenir des coupes plus légères (fuel, gazole, essence) (Figure 1-3). Les différents temps de séjour sont généralement de l'ordre de 1 à 3 minutes pour la viscoréduction et de plus de 24 heures pour la cokéfaction [36]. Étant donné que le PDMS est ajouté dans ces procédés, certains auteurs [4, 30, 32] se sont intéressés aux produits de dégradation du PDMS déjà mis en évidence sous atmosphère inerte [30]. A partir de 300°C, le PDMS commence à se dégrader pour former des siloxanes cycliques (D_3-D_6 majoritairement) [8-10]. A partir des températures d'ébullition des siloxanes cycliques (Figure 1-3), ces composés distilleraient majoritairement dans les coupes naphta et essences. Néanmoins, nous verrons dans ce travail que ces propos sont à nuancer.

De récents travaux au sein d'IFP Energies nouvelles [17, 37] ont apporté des connaissances supplémentaires au niveau de la quantité de Si totale présente dans les différentes coupes. Les coupes C_5-C_6 issues de la cokéfaction (0-80°C) contiennent environ 1 mg de Si.kg^{-1} tandis que les coupes plus lourdes (80°C-70°C) sont beaucoup plus chargées en Si (50 à 80 mg de Si.kg^{-1}). En 2008, Da *et al.* avaient également reporté des concentrations comprises entre 32 et 53 mg de Si.kg^{-1} respectivement pour un naphta de cokéfaction et de viscoréduction [38]. Une synthèse de la composition d'essences de cokéfaction issues de différentes raffineries montre que les teneurs en Si varient entre 0,4 et 40 mg de Si.kg^{-1} mais aucune spéciation (nature et quantité des différentes formes chimiques d'un élément) n'a été effectuée [17]. Les quantités de silicium total retrouvées sont très faibles et nécessitent donc l'utilisation de techniques analytiques sensibles capables de détecter des molécules silicées à des teneurs de l'ordre du µg de Si.kg^{-1}.

1.3.2.2.2 Vapocraquage

Concernant les fractions légères, le vapocraquage est un procédé clé de la pétrochimie. Il permet de produire des oléfines (C_2-C_4) et des aromatiques (benzène, toluène, xylène) sans catalyseur mais en présence de vapeur d'eau (25-50% en masse), entre 820 et 850°C et pour des temps de séjour très courts (0,08 à 1,2s) [39]. Les charges utilisées en entrée sont principalement constituées de coupes naphta (Figure 1-3) ou de fractions légères obtenues à l'issue d'une cokéfaction par exemple [39]. Conjuguée à la dégradation thermique du PDMS, une dégradation en présence de vapeur d'eau (section 2.2.2) s'ajoute dans ce procédé et va également accentuer la formation de composés silicés, probablement de nature chimique différente, qui vont ensuite se retrouver dans les différentes coupes pétrolières en sortie du procédé. De plus, pour réduire le cokage dans ce procédé, des composés phosphatés, soufrés ou encore silicés (tetraéthoxysilane et bis-trimethylsilyl sulfure) sont également ajoutés [40].

Concernant les coupes issues du vapocraqueur, selon des retours d'unités industrielles, les teneurs en Si augmentent également dans les fractions les plus lourdes. Néanmoins, il n'y a pas eu de quantification effectuée par coupe, les teneurs étant généralement en-dessous des limites de quantification par ICP-OES (200 µg de Si.kg^{-1}) au moment des analyses [17]. Désormais, les travaux de Sanchez *et al.* ont récemment permis de porter les limites de quantification à 20 µg de Si/kg quelque soit la matrice pétrolière analysée, soit un gain en sensibilité d'un facteur 10 [41, 42].

1.3.2.3 Procédés de finition : Hydrotraitement (HDT)

L'hydrotraitement désigne l'ensemble des procédés qui visent à éliminer les composés indésirables (Tableau 1-5) présents dans les coupes pétrolières grâce à l'utilisation d'un catalyseur en présence d'hydrogène (20-200 bar) et entre 320 et 390°C. Le but est d'obtenir des produits finis aux spécifications commerciales demandées (qualités et normes de pollution) d'une part, et d'autre part de préparer les charges pour d'autres unités de transformation ou de conversion dont certains catalyseurs sont sensibles aux impuretés.

Concernant l’empoisonnement des catalyseurs d’hydrotraitement, le Si est connu pour être un poison sévère des catalyseurs d'hydrodésulfuration (HDS) [30] et d'hydrodénitrification (HDN) [32]. D'après Didillon *et al.*, [43] il s'agit du quatrième poison retrouvé sur des catalyseurs d'hydrogénation Pd/Al_2O_3 de retours industriels. De nombreux travaux ont été réalisés sur l'empoisonnement par le Si dans les procédés pétroliers et dans la production de biogaz. Ils seront brièvement développés dans la section 1.4 de ce rapport dans le but d'augmenter notre connaissance sur la nature des molécules poisons déjà testées et potentiellement présentes dans les charges.

Tableau 1-5. Différents procédés d'hydrotraitement [24]

Procédés	Composés éliminés	Exemples de réactions	Ex. de Catalyseurs
Hydrodésulfuration	Soufrés	$C_aH_bS + dH_2 \rightarrow H_2S + C_aH_e$	Co-Mo/Al_2O_3
Hydrodénitrification	Azotés	$C_aH_bN + dH_2 \rightarrow NH_3 + C_aH_e$	Ni-Mo/Al_2O_3
Hydrodésoxygénation	Oxygénés	$C_aH_bO + dH_2 \rightarrow H_2O + C_aH_e$	Co-Mo/Al_2O_3
Hydrodémétallation	Organométalliques M= Ni, V, As, Pb, Cu	$C_aH_bM + dH_2 \rightarrow M + C_aH_e$	Co-Mo/Al_2O_3
Hydrogénation	Oléfines, dioléfines, aromatiques	$C_aH_{2b} + dH_2 \rightarrow C_aH_{2b+2}$	Ni-Mo/Al_2O_3

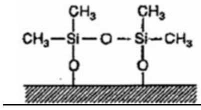
1.4 Impact du silicium

1.4.1 Catalyseurs de l'industrie pétrolière

Dans le domaine des procédés pétroliers, l'état de l'art atteste d'effets très différents de l'empoisonnement de silicium sur les catalyseurs. En effet, plusieurs paramètres tels que la nature du catalyseur (Ni, Pd, Pt), les conditions expérimentales imposées (température, réaction étudiée) et la nature chimique du composé poison jouent un rôle prépondérant sur l'activité, la sélectivité et la durée de vie du catalyseur. Le Tableau 1-6 montre bien qu'une même molécule peut avoir différents effets (promotion ou désactivation) sur le catalyseur. Les composés respectant cette dualité sont illustrés en rouge dans le tableau. Nous pouvons citer l'exemple du triéthylsilane qui provoque un empoisonnement lors de l'hydrogénation du benzène et de différentes oléfines [44-46], mais aussi une promotion de l'activité lors des travaux de Marques *et al.* [47] sur l'hydrogénation du 1,3-Butadiène. D'autre part, un test d'empoisonnement par l'hexaméthyldisilane sur un catalyseur d'hydrogénation au Pd n'avait montré aucun effet néfaste [48] tandis que Nuzzo *et al.* [49] avaient relevé une promotion de l'activité du catalyseur au Ni.

La disparité de l'effet empoisonnant des molécules silicées sur les catalyseurs démontre clairement le besoin de connaître les espèces silicées présentes dans les charges pétrolières en réalisant une spéciation du silicium.

Tableau 1-6. Synthèse des tests d'empoisonnement réalisés sur des catalyseurs d'hydrogénation

Composés	Catalyseur/Réaction	Conditions	Réf.
Empoisonnement confirmé			
	$NiMo/Al_2O_3$ (catalyseur industriel	• HDT de naphta • 320-360°C, 50 bar	[50]
Si total : 32-53 mg de Si.kg^{-1}	$NiMo/Al_2O_3$ (catalyseur industriel)	• HYD de naphta • 350°C, 2,5 MPa	[38]
non renseigné	Pt/Al_2O_3	• Reformage du naphta à 500°C	[51]
Diméthoxydiméthylsilane (DMDS)	Pd ou Ni/Al_2O_3	• HYD sélective du butadiène • 17, 50, 100, 180°C et P_{H2}= 10 bar • 40 ml d'heptane (Conditions F.M.)	[47]
• Triéthylsilane (Et_3SiH) • Silane (SiH_4)	Pd/SiO_2 et Ni/SiO_2	HYD du cyclopentène à 250°C	[44]
Triéthylsilane	Cu, Ni, Rh, Pd, Pt (/Al_2O_3)	• HYD du propène, benzène et 2-propanol • 473 et 673 K	[45]
Triéthylsilane	Pd	HYD du cyclohexène à 250°C	[46]
Méthylsilane (CH_3SiH_3)	Surface en Ni	0°C	[52]
Silane (SiH_4)	Catalyseur à base de Ni/Al_2O_3	Conversion du cyclohexane en benzène et produits d'hydrogénolyse à 300-320°C	[49]
•Couche de SiO_2 •Composés organosilicés	Catalyseur industriel LD265 (Pd/Al_2O_3)	HYD sélective	[43]
Molécules suspectées d'empoisonnement			
PDMS	LD265	150°C, P_{H2}= 30 bar, essence pygas	[53]
PDMS-OH	Pd ou Ni/Al_2O_3	Conditions Marques *et al.*	[47, 54]
Diéthoxydiméthylsilane	Pd/Al_2O_3	200°C, heptane, 24 heures	[55]
Hexaméthyldisilane ($C_6H_{18}Si_2$)	LD265	17°C, P_{H2}= 10 bar, 4 heures	[48]
Tétraéthoxysilane $Si(OC_2H_5)_4$	Alumine SCM129	éthanol, 60°C, 1h, Séchage, 110°C, 1 nuit, Oxydation, 500°C, 12h	[56]
• Tétraméthylsilane, $(CH_3)_4Si$ • Triméthylsilane, $(CH_3)_3SiH$ • Silacyclohexane	Surface Pd(110)	Déshydrogénation du cyclohexène	[57]
Tétraéthylsilane ($SiEt_4$)	Ni/Al_2O_3	80°C et heptane	[58]
Promotion de l'activité			
• D_4 et PDMS-OH • Triéthylsilanol • Triéthylsilane	Pd ou Ni	Conditions Marques *et al.*	[47]
Silane (SiH_4)	HYD de l'acétylène	250°C	[59]
• Silane (SiH_4) • Hexaméthyldisilane	Ni/Al_2O_3	• 300-320°C • Conversion du cyclohexane en oléfines	[49]

HDT : hydrotraitement; HYD : hydrogénation; PH_2 : pression d'hydrogène

1.4.2 Autres problèmes engendrés par le Si

L'industrie pétrolière n'est pas le seul domaine industriel concerné par la présence de composés silicés indésirables. En raison de leur utilisation courante dans de nombreuses applications, les composés silicés se retrouvent dans l'environnement, les boues de station d'épuration, les déchets à incinérer et le biogaz [60] dans lesquels ils posent des problèmes au niveau des turbines et au niveau du traitement catalytique des gaz. En effet, la présence de composés silicés dans le biogaz entraîne la formation d'une couche de silice abrasive (SiO_2) qui affecte considérablement la durée de vie des moteurs et des autres éléments (pistons, turbines, bougies) [61].

Au niveau du traitement catalytique des gaz, les problèmes d'empoisonnement sont similaires à ceux décrits pour l'industrie du raffinage. De nombreux travaux pour comprendre l'empoisonnement par le Si ont été reportés lors de l'oxydation des composés organiques volatiles (COV) [62-67] et lors de l'utilisation de capteurs catalytiques [68, 69] pour la détection de gaz inflammables. L’hexaméthyldisiloxane (L_2) est le composé choisi comme molécule empoisonnante modèle dans ces études car il s’agit du poison le plus sévère testé pour ce type de catalyseur (Pt et Pd) [64-67].

Au sein de l'industrie automobile, plusieurs phénomènes d'empoisonnement par le Si sur des sondes et des capteurs présents sur les véhicules ont été reportés [70, 71]. En effet, en 1985, des échantillons d’essences sans plomb contenant 30 à 110 $mg.kg^{-1}$ de Si ont posé de sérieux problèmes sur les sondes à oxygène de nombreux véhicules. Il semble que l’utilisation de toluène contaminé et recyclé de l’industrie des semi-conducteurs pour augmenter l’indice d’octane soit à l’origine de ce problème d’empoisonnement [70]. Ce même phénomène s’est également déroulé au Royaume Uni en 2007 avec 400 000 véhicules à l’arrêt du fait de la formation d’une couche de silice sur les sondes à oxygène des voitures [71].

1.5 Conclusions du Chapitre 1

Le but de cette partie était de définir la composition des produits pétroliers et de déterminer l'origine et l'impact du silicium au sein des différents procédés pétroliers. Le silicium provient majoritairement de la dégradation thermique des agents antimousse de type PDMS ajoutés dans les différents procédés de distillation et de conversion. Les conditions appliquées dans les différents procédés sont cruciales et vont probablement entraîner la formation de composés silicés de nature chimique différente et totalement inconnus.

Cet élément va donc potentiellement se retrouver dans les différentes coupes pétrolières dirigées ensuite vers les procédés d'hydrotraitement dont les catalyseurs sont sensibles au silicium. Pour le moment, les coupes naphta et essences sont les fractions dans lesquelles le silicium est principalement retrouvé. En effet, les concentrations mesurées par ICP-OES sont comprises entre quelques centaines de µg.kg^{-1} (ppb) et quelques mg.kg^{-1} (ppm) dans ces différentes charges. Néanmoins, la présence de silicium dans les autres coupes pétrolières n'est pas à exclure.

Les tests d'empoisonnement effectués avec des molécules modèles montrent différents effets sur la performance d'un catalyseur pour une même molécule. Afin de disposer d'une liste exhaustive de molécules silicées, les espèces déjà testées mais n'ayant pas montré d'effet poison dans ces travaux seront tout de même prises en compte dans notre étude. Il est donc crucial de réaliser une spéciation du silicium dans les charges d'hydrotraitement pour connaître les composés présents afin de comprendre et de limiter l'empoisonnement des catalyseurs. Avant ce travail de thèse, seul un dosage total du silicium était effectué dans les produits pétroliers. Aucune information sur la nature chimique des composés silicés présents dans les charges n'a donc été reportée.

Dans l'optique de choisir une ou plusieurs techniques analytiques pour la spéciation du silicium, le Chapitre 2 propose une étude bibliographique complète sur les techniques d'analyse reportées pour cet élément dans différents domaines (environnemental, biologique et industriel). L'analyse du silicium total et les possibles problèmes de contamination sont également abordés mais le cœur de ce travail est focalisé sur les techniques utilisées pour la spéciation du silicium dans ces différents domaines. Le potentiel et les limitations des différents outils analytiques sont particulièrement soulignés. Suite à une invitation, ce travail a été précédemment publié dans une issue spéciale de **Journal of Analytical Atomic Spectroscopy** (J. Anal. At. Spectrom) portant sur la spéciation en 2011.

Chapitre 2. Silicon speciation by hyphenated techniques for environmental, biological and industrial issues: A review

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CRITICAL REVIEW

Silicon speciation by hyphenated techniques for environmental, biological and industrial issues: A review†

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Silicon speciation in environmental, biological and industrial matrices is of considerable importance due to its wide use in many consumer and personal care products and industry. In addition, the entry of silicones in various compartments like wastes, soils, air and water highlights the need to perform exposure studies, toxicological surveys and to measure negative effects. Due to possible contamination and trace level presence of silicon compounds, challenges to determination, identification and quantification are presented. The principal species of concern include siloxanes, silanols, silanediols and silanes. State of the art of analytical methods for total silicon determination and silicon speciation are established. Atomic spectroscopic methods are mainly used to measure total Si at trace concentration levels. On the opposite, hyphenated techniques are performed for Si speciation. Particular attention is paid to chromatographic methods coupled to sensitive and selective detectors (MS, AED and ICP) allowing structural information. Liquid and gas chromatography emerge as the most widespread separation techniques. However, other procedures such as MS, NMR, IR and XRF enable a better knowledge of these species. The potential and limitations of hyphenated techniques are highlighted, particularly concerning sensitivity and selectivity. Furthermore, potential sources of contamination and analytical artifacts in silicon determination are reviewed.

2.1 Introduction

Organosilicon compounds such as siloxanes and polydimethylsiloxanes (PDMS) are widely used in a variety of industrial applications and consumer goods since their commercial introduction in 1943 [72]. These molecules find their applications in a wide array of common consumer products such as cosmetics, textiles, medicinal implants, pharmaceuticals, chemistry and in industry (lubricants, coatings, gels, adhesives, antifoaming agent...) [61, 73, 74].

Silicon species used in these applications are polymeric silicon organo compounds formulation consisting of a backbone of alternating Si-O units with organic side chains attached to each silicon atom [73]. These structures provide the species with unique high thermal stability, low surface tension, hydrophobicity, electric insulation, and lubrification properties [74]. These specificities resulted in the fact that some siloxanes have been identified as High Production Volume (HPV) chemicals by the US Environmental Protection Agency (USEPA) [75] and by the Organisation for Economic Co-operation and Development (OECD) [76]. HPV products are defined as compounds produced or exported exceeding 1000 tons per year in at least a region or a country [76]. As a result of their every wide usage, these different products are dispersed in the environment and are present in a large variety of biological and industrial matrices (petroleum and derived petroleum products) most frequently at trace levels. Their ubiquitous occurrence in the environment requires the silicon species to be investigated to assess their environmental fate [73, 77]. Both the ecological [78] and toxicological impact of the silicon [79, 80] have been recognized to be of concern therefore, it is necessary to carry out exposure and effects studies of the species [81-83]. In order to improve the general knowledge of the occurrence, pathways and toxicity assessment of silicon species, speciation of silicon and their species must be undertaken to improve the understanding of their impact and translocation in the environment.

According to the International Union of Pure and Applied Chemistry (IUPAC), speciation is defined as the analytical process that leads to measure the distribution of an element specific chemical species in a sample [19]. Silicon speciation is gaining interest and addresses the identification and quantification of the physical and chemical forms of silicon [20].

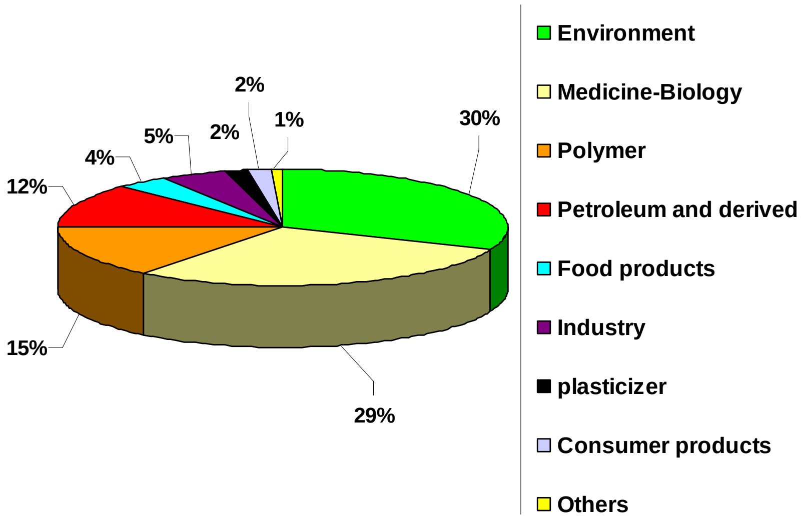


Figure 2-1. Publication distribution in percentage for silicon determination and speciation in different application domains

The developing domain of silicon speciation is being reviewed and Figure 2-1 presents the number of publications for Si determination and speciation in its different application domains. This figure shows that environment, medicine, biology polymer synthesis and petroleum applications are the most investigated fields of interest. Two main books deal with the analytical chemistry of silicones [72, 84] but more specifically on total Si determination.

Also a review was published in 2006 by Varaprath *et al* on silicone analysis and its artifacts in environmental and biological samples [85].

However, silicon speciation as such is not well developed and the number of articles is small. Silicon is in general present at very low concentrations in most of the investigated matrices [86, 87]. Further, contamination problems during the entire analytical procedure [88] as well as in the artifacts [89, 90] generates a real analytical challenge. The reason being that due to their widespread use of silicon species in many products, their stability and of the high reactivity of certain silicon species which may alter the analytical process. Therefore, a wide variety of high-performance analytical techniques have been developed and applied. Figure 2-2 summarises the results of a general survey of more than 120 articles published over the last 30 years dealing with total silicon determination methods as well as the hyphenated techniques applied for silicon speciation.

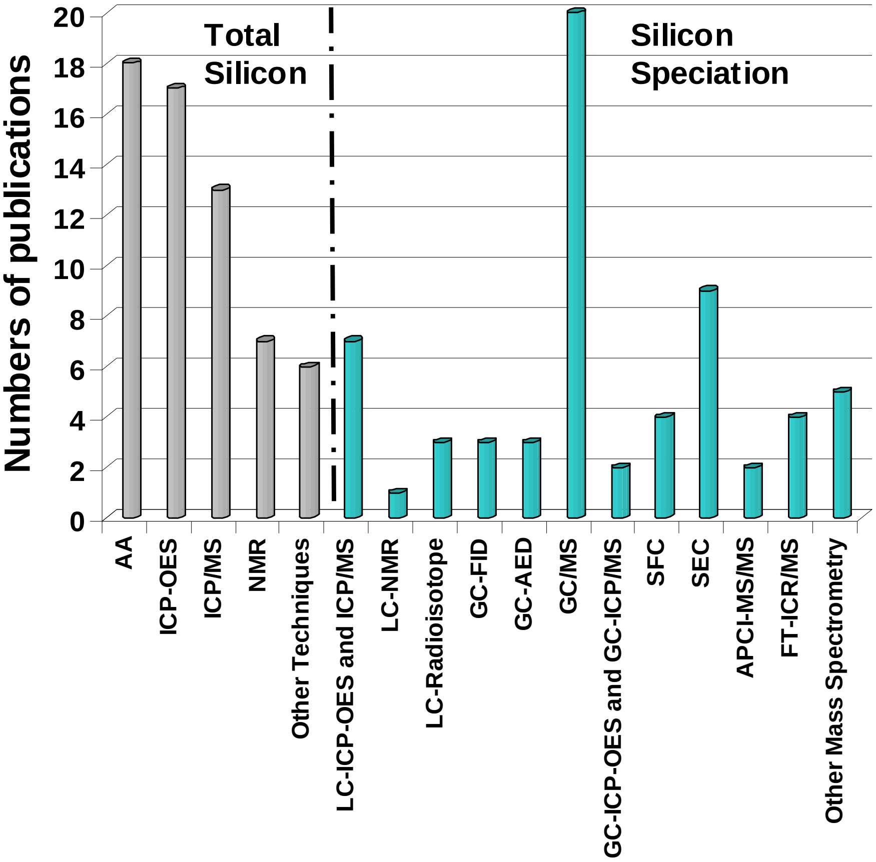


Figure 2-2. Number of publications for silicon determination and speciation by different methods

The objective of this article is to review the main analytical methods used for silicon determination and silicon speciation in environmental, biological and industrial applications. One section is focused on contaminations and analytical artifacts which in the case of silicon is of special concern for the validity of the data and has been a major drawback for the development of this analytical domain. In general, direct analytical methods based on atomic spectroscopic methods (AAS, ICP-OES and ICP/MS) and also NMR techniques give access to total silicon measurement. All the direct spectrometric methods do not provide information about silicon speciation (Figure 2-2). Silicon speciation relies on hyphenated techniques combining the high separation potential of chromatography (*e.g.* LC or GC) with identification possibilities offered by mass spectrometry (MS) or the sensitivity and selectivity of an element specific detector (AED, ICP-OES and ICP/MS). This review is mainly focused on silicon speciation by hyphenated techniques particularly at trace concentrations compared to classical total determination methods for silicon. Special attention is given to the contamination problems encounter during the entire analytical process which in this case is of particular relevance for the data quality.

2.2 Molecules, fields of interest and analytical methods

2.2.1 Organosilicon compounds

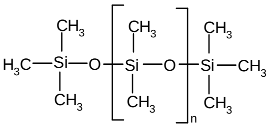
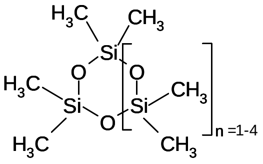
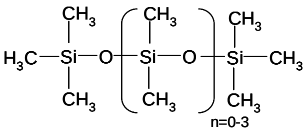
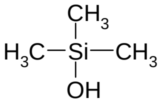
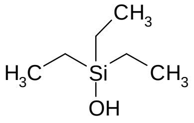
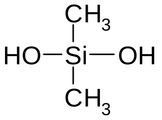
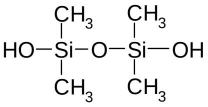
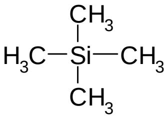
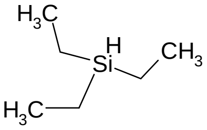
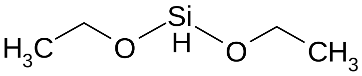
The present paper deals with siloxanes (cyclic and linear), silanols (trimethylsilanol), silanediols (dimethylsilanediol) and silanes. These correspond to the four main families of organosilicon species (Table 2-1) found in the fields of interest reported in Figure 2-1 [91]. As siloxanes have long names, abbreviations created by Hurd [92] are employed for several species such as D_n (Table 2-1). Siloxanes are typically represented by the following letters "M, D, T, Q" which correspond to the number of oxygen linked to an atom of silicon. Indeed, M indicates a silicon linked to one oxygen, while D, T, Q indicate a silicon linked to two, three and four oxygens respectively. Moreover, Table 2-1 lists formula, molecular mass, boiling point and structure of species according to the fields of interest presented in Figure 2-1.

2.2.2 Fields of interest

PDMS, defined as a High Molecular Weight (HWM) polymer is the most important silicone used for industrial and consumer applications (80%) [73]. Other silicones are mainly of Low Molecular Weight (LMW) materials, also referred to as Volatile MethylSiloxanes (VMS) with significant vapour pressures under ambient environmental conditions [83, 93].

Consequently, the behaviour of HMW and LMW siloxanes has gained in interest in many matrices. The following paragraphs report problems caused by these species.

Table 2-1. Molecules of interest

Silicon species (Hurd Abbreviations)	Formula	MM (g.mol^{-1})	B.P (°C)	Structure	Fields of Interest *
Siloxanes					
Polydimethylsiloxane (MD$_n$M)	PDMS viscosity : 12,500 cSt	67,700	—		EN
Hexamethylcyclotrisiloxane (D$_3$) Octamethylcyclotetrasiloxane (D$_4$) Decamethylcyclopentasiloxane (D$_5$) Dodecamethylcyclohexasiloxane (D$_6$)	$C_6H_{18}O_3Si_3$ $C_8H_{24}O_4Si_4$ $C_{10}H_{30}O_5Si_5$ $C_{12}H_{36}O_6Si_5$	222 296 370 382	134 175 211 245		BI BF CP
Hexamethyldisiloxane (MM) or L$_2$ Octamethyltrisiloxane (MDM) or L$_3$ Decamethyltetrasiloxane (MD$_2$M) or L$_4$ Dodecamethylpentasiloxane (MD$_3$M) or L$_5$	$C_6H_{18}OSi_2$ $C_8H_{24}O_2Si_3$ $C_{10}H_{30}O_3Si_4$ $C_{12}H_{36}O_4Si_5$	150 236 310 382	100 153 194 210		P PP
Silanols					
Trimethylsilanol (TMS)	$C_3H_{10}SiO$	90	99		EN
Triethylsilanol (TES)	$C_6H_{16}Osi$	132	158		PP
Silanediols					
Dimethylsilanediol (DMSD)	$C_2H_8O_2Si$	92	102		EN PP
Tetramethyl-1.3-disiloxanediol (TMSD)	$C_4H_{14}O_3Si_2$	166	—		EN
Silanes					
Tetramethylsilane	$C_4H_{12}Si$	88	27		EN PP
Triethylsilane	$C_6H_{16}Si$	116	107		PP
Diethoxydimethylsilane	$C_5H_{14}O_2Si$	134	95		PP

* EN: Environmental samples (air, soil, water, sediments); BI: Breast implants; BF: Biological fluids; CP: Consumer products; P: Polymers; PP: Petroleum and derived products

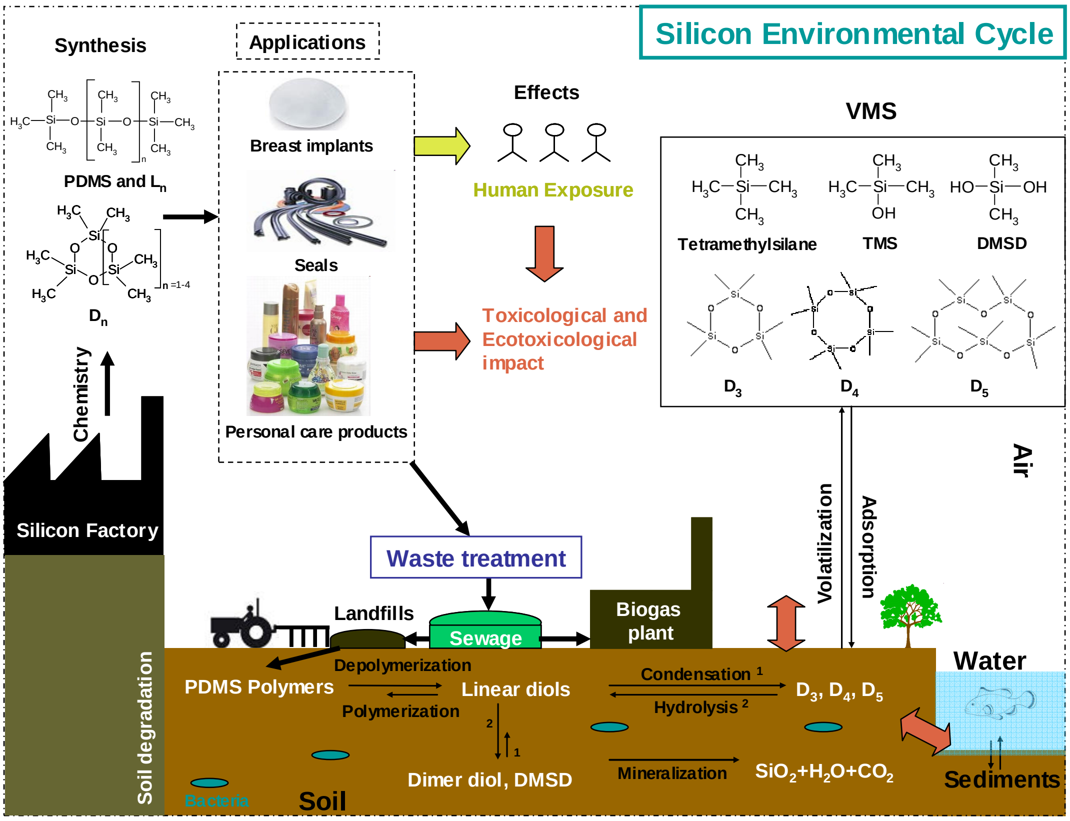


Figure 2-3. Fate of silicon in the environment

Environment: The entry of silicones into the environment may also occur from applications resulting with wastes and volatilization (Figure 2-3). As a result of their wide use, VMS (D_n and L_n) evaporate into the atmosphere [94, 95] and degrade in the soils [96]. Additionally, some of these species can be produced by PDMS degradation in environmental conditions. Due to low solubility in water and high adsorption coefficient [77], PDMS ends up and degrades in landfills sewage [97-99], biogas [61, 100] soils, [77, 90, 101-103] and sediments (Figure 2-3) [104]. The dimethylsilanediol (DMSD) is the main degradation product obtained by PDMS hydrolysis [77, 101, 103, 105]. Then, it can be evaporated due to its high vapour pressure and oxidized by radicals as the other volatile species found in environment (tetramethylsilane, trimethylsilanol (TMS), L_2 and D_3-D_5) [106-108]. Subsequently, this compound is biodegraded in soils where it is mineralized in end products (CO_2, SiO_2 and H_2O) (Figure 2-3) [77]. Buch and Ingebringston have also shown the formation of low molecular oligomers (siloxanes and silanols) during PDMS degradation [109]. In addition, Carpenter *et al.* [110] reported the presence of monomerdiol (DMSD), traces of dimer and trimerdiols, octamethyltrisiloxane (L_3) and TMS during PDMS degradation in soils by hyphenated techniques.

LMW hydrolysis products are water soluble and volatile. Thus, these induce silicon molecules which can partition from the soil to the water and into the atmosphere (Figure 2-3) [77]. In addition, combustion of silicon containing biogas produces the abrasive silica and causes serious damages to gas engines [61, 111], heat exchangers [112], and catalytic exhaust gas treatment [64].

Long *et al.* [113] have developed a novel onsite method for siloxane detection in biogas based on microcantilever array use. Performance like high sensitivity, portability, inexpensive and less energy consuming than GC/MS promise to facilitate in-field siloxane analysis and reduce biogas cost [113]. Several applications are performed to reduce and eliminate silicon species in biogas [114, 115]. Silicon speciation in the environment contributes to estimate the environmental fate and the ecological and toxicological risks occurred by siloxane compounds in vulnerable ecosystems [78] (Figure 2-3).

Medicine and biology: PDMS is employed in silicone gel-filled breast implants (Figure 2-3) for aesthetic surgery because it was supposed to be biologically inert [116]. This gel contains 98% of HMW and only 1-2% of LMW silicones (D_3-D_7) [117]. Lykissa *et al.* reported that D_5-D_7 are the most concentrated of LMW molecules content in silicone implant gel [118]. These compounds can be released in blood [117], plasma [117] and tissues [118, 119] of human exposed to breast implants. Consequently, sensitive techniques have been used to quantify silicones in order to carry out epidemiologic studies [117-120]. Currently, there is no credible correlation between the increase of diseases such as cancer originating in the breast among women with cosmetic breast implants [121, 122].

Consumer products: VMS siloxanes such as D_n and L_n are mostly used in consumer products (Figure 2-3). Two recent works achieve the determination of organosilicon compounds levels in personal care and cosmetic products such as fragrances, hair care products, antiperspirants, skin lotions, baby products and many other consumer goods [82, 83]. These results show that more than 50% of the investigated samples contained D_4, D_5 and D_6 [82]. Cyclic molecules were predominant compared to linear siloxanes. Wang *et al.* [83] have also reported that D_3, D_4, D_5 and D_6 are respectively found in 0.8, 4.8, 14.3 and 9.1 percent of the analyzed products Considering these studies [82, 83], D_5 is the most abundant compound (680 $mg.g^{-1}$ in an antiperspirant) [83]. Regarding their high concentrations, one can wonder if a potential adverse effect can happen [82]. According to Wang *et al.* [83], no risk for dermal exposure of these products has been identified because of two reasons: firstly the uncertainty in adsorption efficiency penetration rates in human skin and secondly in the evaporation during products use [83]. However, speciation is necessary to subsequently perform exposure studies to silicon compounds such as occupational exposure assessment in silicon industry [123], exposure to ambient atmosphere [94, 95] and exposure per D_4 inhalation [81] (Figure 2-3). Furthermore, fertility problems can occur during D_4 exposure of animals [79, 80] as well as potential carcinogenicity after rats exposures to D_5 [124].

Polymers: Due to the need of polymer synthesis enhancement, several workers have carried out studies dealing with PDMS stability [8, 9, 11]. Experiments have been performed using thermogravimetric analysis (TGA) and GC/MS at high temperature and under helium flow for polymer applications like rubbers, insulating materials or ceramics. Figure 2-4 illustrates the distribution of D_n compounds generated by the degradation of PDMS between 400 and 500°C in three different publications [8, 9, 11]. The production of D_n tends to decrease as the polymerization degree increases. As shown in Figure 2-4, LMW siloxanes (D_3-D_6) are the major compounds. Moreover, Camino *et al.* suggested that mixtures obtained by the degradation in presence of air is similar to that one under He flow [11]. However, many other molecules can be generated by decomposition according to temperature, oxygen levels [10, 11], impurities [9, 125] and polymer terminal group [126, 127].

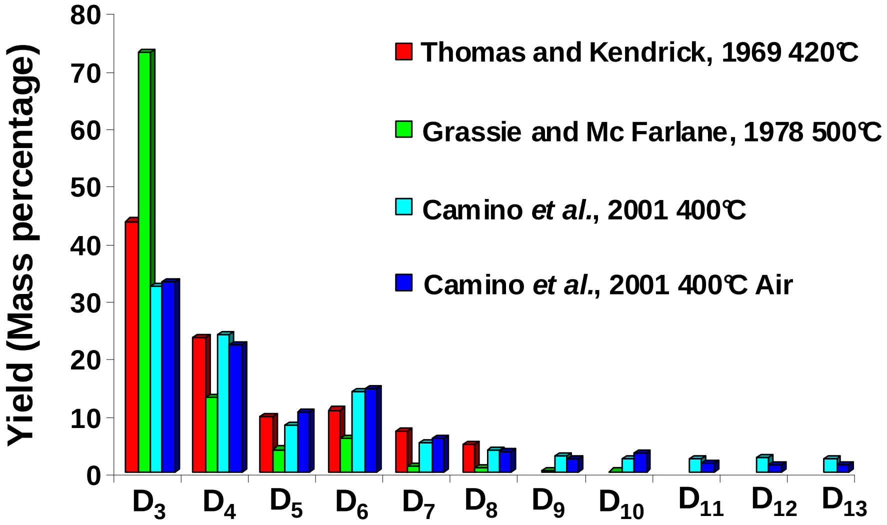


Figure 2-4. Low molecular cyclic siloxane (D_n) distribution generated during PDMS degradation at different temperature (mass percentage)

Petroleum and derived products: This field is also concerned by silicon contamination due to the fact that causes catalyst poisoning in refining processes and in particular in hydrotreatment [2] (Figure 2-5). In addition, automobile and fuel sensors as well as emission control devices are susceptible to silica poisoning because of contamination from fuel [70]. Indeed, in 1985, samples of unleaded fuels with concentration ranging between 30 to 110

$mg.kg^{-1}$ of Si caused troubleshooting in motor engine combustion [70]. Even if the origin was not well established, one hypothesis consists in the unintentional use of recycled and contaminated aromatic process solvent (toluene) used as octane booster by area fuel blenders [70]. Similarly, this phenomenon occurred once again in United Kingdom in 2007 with 400,000 damaged cars due to the formation of silica layer on an O_2 probe in automobile sensors.

Silicon presence in feedstocks is derived from antifoaming agents (PDMS), added in the lighter fractions of coker or visbreaker operations [30, 50]. Figure 2-5 presents a petroleum process constituted of feed thermal cracking (coker and steam cracker), separation and hydrogenation units. Due to the PDMS degradation, silicon compounds (Table 2-1) are found at trace levels [15, 16] in feeds and occur as poison which induce severe catalytic deactivation by adsorption on the catalyst surface [38, 43, 45, 50, 51, 128] (Figure 2-5). According to theoretical explanations and GC analysis of heated silicon oil, several authors suggest that cyclic oligomers (D_n) are the major breakdown products of PDMS released in petroleum products [30, 32]. These explanations are in agreement with results presented in Figure 2-4 [8, 9, 11] due to the high temperatures in petroleum processes [30]. According to Breivik and Egebjerg [32], cyclosiloxanes are rapidly adsorbed on the catalyst surface of hydrotreatment and caused catalyst deactivation. In addition, Molnar *et al.* [45] demonstrated a poisoning of olefin hydrogenation by triethylsilane between 200 and 400°C. Furthermore, recent studies have shown poisoning by hexamethyldisiloxane (L_2) used as a model poison compound during combustion of volatile organic compounds (VOC) in gas treatment [64-67]. These phenomena give rise to untimely catalyst replacement and economic loss. Consequently, the petroleum industry must continuously propose sensitive analytical methods in order to reach the specifications in petroleum products [129]. As far as demonstrated in the literature, only a total determination of Si is achieved in petroleum matrices [130, 131]. However, speciation (identification and quantification) is necessary to give access to the chemical nature of poison species and hence, a better understanding of the poisoning processes.

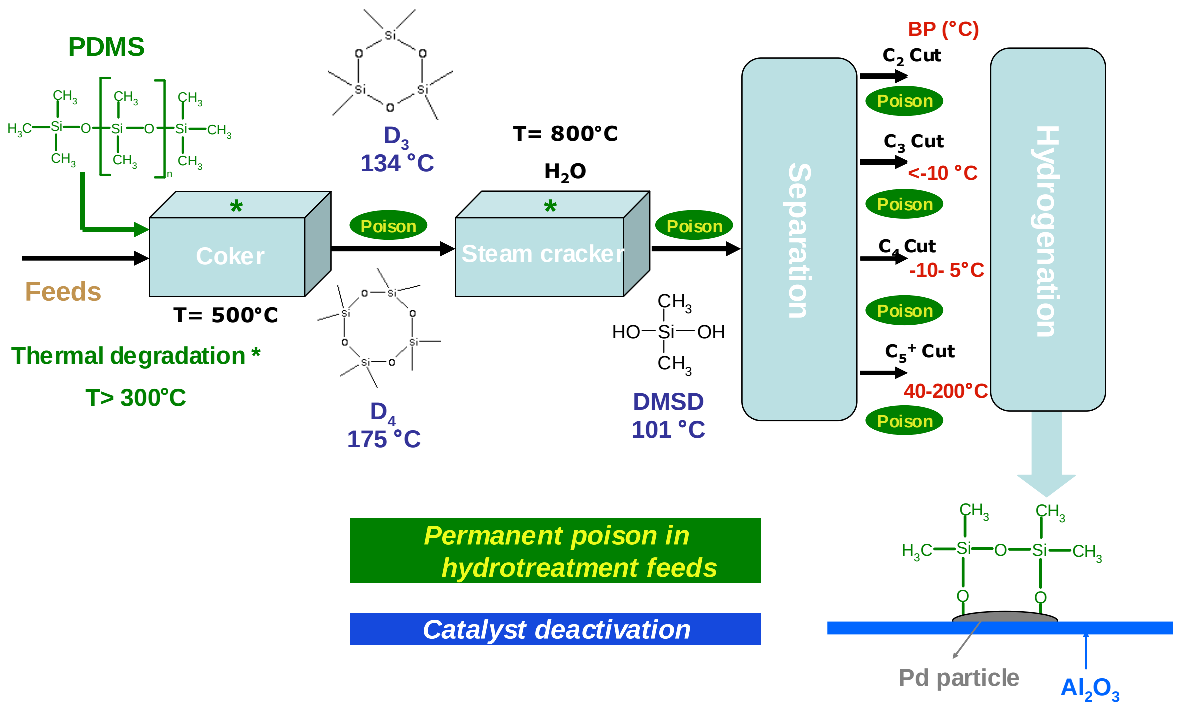


Figure 2-5. Silicon poisoning in petroleum process

2.3 Analytical methods for silicon determination and speciation

As previously mentioned, silicon compounds result in numerous problems in the environment (fate and exposure), medicine and biology (breast implants), consumer products (exposure, toxicity), polymers (stability) and catalysts (poisons) in petroleum processes and gas treatment. Consequently, two different groups of techniques used for silicon determination, are presented in Figure 2-6. These techniques consisted of direct analysis to achieve total silicon determination as well as, hyphenated techniques for silicon speciation. Before selecting an analytical method, it is essential to define the matrix, the species and compound concentration ranges especially at trace levels [85]. Generally, detection limits greatly depend on the preparation and one concentration. Thus, comparison between different technique performances is difficult.

Most total silicon determinations are performed by atomic spectroscopy, NMR and other methods by infra-red spectroscopy (IR) and X-Ray fluorescence (XRF) (Figure 2-6). For silicon speciation, MS methods and SEC separation have been usually employed for HMW molecules. On the other hand, the methods on the right side of Figure 2-6 are used for LMW compounds. Silicon speciation requires chromatographic separation (LC, SFC and GC) coupled to a suitable detector depending on the expected detection limit. The survey presented in Figure 2-2 clearly shows that GC/MS is the most commonly employed hyphenated technique for trace level Si speciation. Flame ionization detector (FID) can also be applied but it does not provide very low detection limits. The coupling of GC and atomic detection such as AED or ICP (inductively coupled plasma) allows high sensitivity and selectivity therefore, giving access to structural information. The combination of LC and ICP is also used for the determination of a wide variety of silicon compounds as well. MS methods can also be applied to LMW compounds (Figure 2-6) providing identification compared to direct methods.

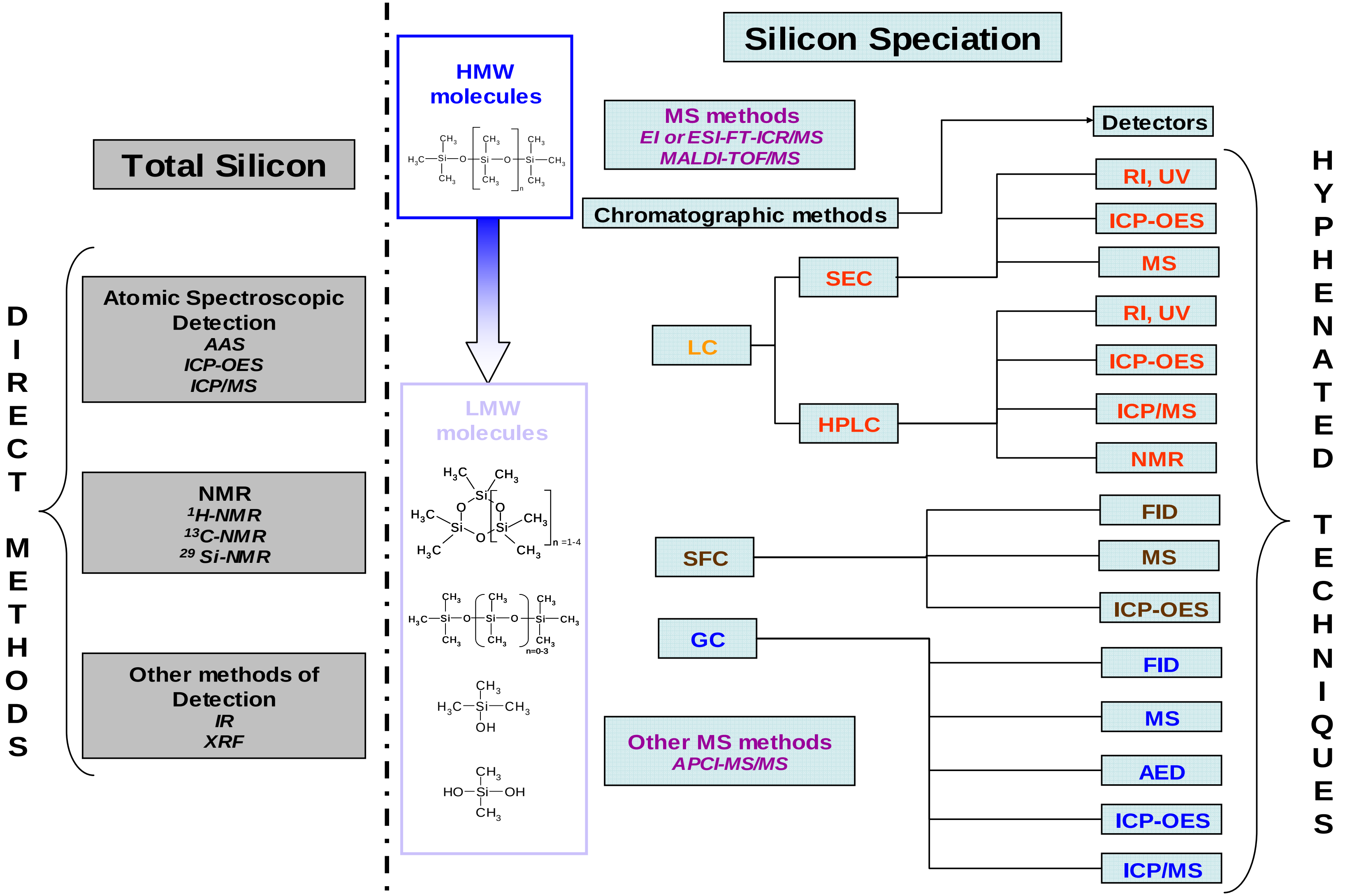


Figure 2-6. Analytical methods for silicon determination and speciation

2.4 Direct methods for total silicon determination

Total silicon can be determined by atomic spectroscopic methods and NMR (Figure 2-2 and Figure 2-6). The major techniques employed for silicon trace analysis are AAS, ICP-OES and ICP/MS. This chapter is mainly focused on environmental, biological, crude oil and derived samples and more particularly on papers published since 2006 for the first two fields. Other studies in environmental and biological fields have also been reviewed in The Analytical Chemistry of Silicones [84] and in Organosilicon Materials [72] but also in a comprehensive review on the analytical aspects of silicones published in 2006 [85].

2.4.1 Atomic spectroscopic methods

These methods can be applied with a decomposition step before silicon determination in order to use in aqueous matrices or directly by injection of organic phases without initial sample digestion. This preparation step is mainly used for solid samples [132-136] and to limit carbon introduction in the plasma [15] allowing minimum mass interferences especially with ICP/MS.

2.4.1.1 Atomic Absorption Spectroscopy (AAS)

GFAAS (graphite furnace atomic absorption spectroscopy) is usually used for silicon determination mainly in environmental and biological matrices with detection limits generally reported below 1 mg.kg^{-1}. However, atomization optimization step is crucial because of possible formation of thermally stable silicon carbide and $SiO_{(s)}$.

The detection of organosilicon materials in river sediments has been reported by AAS after extraction and concentration [104]. More recently, Mukhtar and Limbeck [137] developed an accurate procedure for trace silicon detection in solid environmental samples such as soils or airborne particulate matter using GFAAS. Based on a preliminary treatment of samples leading to a mineralization and with the use of 20 µL sample injection volume, an instrumental LOD of 52 µg.L^{-1} was obtained, which translated to method detection limits of approximately 0.52 µg.m^{-3} when considering collected air volumes [137].

AAS is also applied in medical fields in order to measure concentrations in tissues, plasma and human blood exposed to breast implants [138]. Indeed, the concentration of Si in blood of women with silicone gel-filled breast implants was found to be double (33.5/17.1 µg.L^{-1}) that a women with no implants [139]. Lugowski *et al.* detected Si in blood and urine of individuals exposed to breast implants [140] and in human tissues [88] with µg.L^{-1} levels by GFAAS.

Detection limit (2SD) of 0.5 mg.kg^{-1} of tissue was obtained by GFAAS after heptane extraction [141]. GFAAS has also been employed for silicon measurement in biological tissues as well [142-145]. Hornung and Krivan [144] showed that pre-ashing solid samples improved detection limits (0.2 to 0.03 mg.kg^{-1}), sample homogeneity and precision compared to direct sampling by this previous technique. Moreover, a sensitive (LOD of 1.5 µg.L^{-1}), simple and accurate method for the routine determination of trace silicon by Zeeman GFAAS has been reported [146].

The first technique used in metal trace analysis of petroleum products is GFAAS with detection limits usually reported in the range of 10 µg.L^{-1} [15]. Amaro and Ferreira determined silicon determination in naphtha (C_4-C_{15}) by GFAAS after sample dilution in toluene [130]. An experimental design has been achieved to determine optimal conditions for Si determination to obtain detection limit of 15 µg.L^{-1} [130]. Nevertheless, problems related to the formation of thermally stable silicon carbide ($SiC_{(s)}$) and volatile $SiO_{(s)}$ during pyrolysis by GFAAS can occur [130, 147-149]. These constraints can be resolved by using chemical modifiers [132, 150, 151] or treated Zr tubes [137] to avoid analyte reactions with graphite. Finally, several studies in food products [151-153] with detection limits ranging between 7 µg.L^{-1} and 1.8 mg.L^{-1} and industrial applications (LOD of 30 µg.kg^{-1}) [132] have been carried out by AAS with a pre digestion in order to measure silicon levels.

2.4.1.2 Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES)

ICP-OES can be used for Si determination in environmental, biological and petroleum samples. However, detection limits varied from 3 µg.kg^{-1} and 30 mg.kg^{-1} and depending on sample preparation such as acid digestion. In addition, this latter step avoids spectral interferences observed by ICP/MS.

ICP-OES is a useful tool for environmental samples [154, 155] such as water [156] and agriculture matrices [157]. For instance, the detection of total silicon has been achieved in rivers and sediments by ICP-OES after an extraction of organosiloxanes in a mixture of petroleum ether/MIBK with detection limit of 100 µg.L^{-1} [158] and 10 µg.kg^{-1} [159] of Si respectively. Masson *et al.* [154] reported quantification of Si in plant samples after digestion using samples (2 mg) issued from an inter-laboratory test with detection limit of 30 µg.kg^{-1}. More recently, silicon concentration was measured by this technique in marine sediments as a function of pH and salinity [155]. The results have shown a reduction of silicon levels while the pH increases.

This spectroscopic method was also applied for silicon determination in biological samples such as urine [160, 161], blood [161], tissues and organs [133, 134], plasma [161] and serum [161]. Detection limits of 2 mg.kg^{-1} and 3.7 mg.kg^{-1} obtain by ICP-OES for tissue after digestion using 0.1 g of sample have been reported by Hauptkorn *et al.* [133] and McConnell *et al.* [134] respectively. In 2003, Jia *et al.* [162] obtained a detection limit of 0.2 mg.kg^{-1} during the analysis of silicone oil extracted in a mixture of toluene/ACN in pharmaceutical matrices by ICP-OES coupled with an ultrasonic nebulization. Low silicon concentrations in foods and soils are determined using the association of a microwave dissolution and an ICP-OES [163]. Detection limits have been improved by a factor of 2 with the incorporation of tertiary amines in the acid digestion procedure [163]. Silicon measurement was also achieved by ICP-OES after a microwave acid digestion of foods and beverages due to the importance of Si in bone formation and connective tissue metabolism [164].

In 1988, Carduner *et al.* [70] determined the presence of silicon in petroleum samples and more particularly in unleaded gasolines by ICP-OES with detection limit of 100 µg/L for Si. Botto [131] reported LOD and RSD precision for Si by ICP-OES using two nebulization systems Pneumatic and Ultrasonic Nebulization (USN). The use of ultrasonic nebulization improved the detection limit by a factor of 10. Silicon has been detected at 2.7 µg.kg^{-1} in toluene with an USN system and at 27 µg.kg^{-1} with a pneumatic system. Toluene was an excellent diluent for oil and derived samples. Sanchez *et al.* [165, 166] recently worked on silicon compounds determination by ICP-OES in xylene matrices. The effect of silicon chemical form was evaluated for sixteen different silicon molecules with sensitivity varying by a factor of up to 20 [165]. It was due to the liquid sample introduction system configuration, in particular the spray chamber design. These studies have shown that the application of two introduction systems, heated torch integrated sample introduction system (h-TISIS) [165] and demountable direct injection high efficiency nebulizer (d-DIHEN) drastically reduce the influence of the chemical compound form [166]. In addition, the response of silicon compounds also depends on the matrix but it less pronounced for high dilution factors [167]. Finally, the determination of silicon, iron and vanadium was carried out in petroleum coke by microwave plasma torch atomic optical spectrometry (MPT-OES) after dissolution in nitric acid [168]. This method allows a better control of trace elements which it is very important by using petroleum coke as an electrode.

2.4.1.3 Inductively Coupled Plasma with Mass Spectrometry (ICP/MS)

A significant enhancement of detection limits for silicon can be obtained by replacing OES for MS [16]. Indeed, the performance of ICP/MS allows the detection of very low concentrations levels (sub-ng.L^{-1}) in environmental, biological, petroleum products and in industrial samples. However, molecular interferences can also occur especially for silicon at m/z 28 ($^{12}C^{16}O^+$ and $^{14}N_2^+$) but this problem can be solved with the use of collision-reaction cell [136, 137, 169] or also by using a ICP/HRMS detection [170].

A procedure using a chromatographic purification coupled to Multi Collector (MC) ICP/MS has been described to enable dissolved silicon measurement in natural waters [171]. Silicon isotopic measurement was also achieved by MC-ICP/MS in lake waters [172]. The determination of Si by laser ablation (LA) ICP/MS and X-ray fluorescence (XRF) are also compared for airborne particulate matter [173]. These results emphasized that LA-ICP/MS is the most preferable choice regarding detection limits and matrix limitations.

Several workers have carried out surveys using a microwave digestion before ICP/MS analysis of silicon in biological solid samples [174-176]. Direct determination of Si by a double focusing magnetic sector inductively coupled plasma mass spectrometer without preparation step was reported in serum [177]. Si measurements were carried out using the major ^{28}Si isotope and with a resolving power of 3000, which is sufficient to avoid spectral interferences from $^{14}N_2^+$ and $^{12}C^{16}O^+$ during organic product injection. An interlaboratory trial have been achieved by many co-workers for the determination of silicon in biological samples [176]. Various techniques (ETAAS, XRF, ICP-OES and ICP/MS) were compared considering LOD, RSD and statistical results for each technique and for each matrix.

Due to numerous matrix effects with the introduction of organic samples in ICP/MS, the use of high dilution is recommended [16]. The detection of silicon in naphtha and petroleum matrices after dilution by 10 in toluene has been achieved using a near cold plasma ICP/MS [178]. Sub-µg.kg^{-1} detection limits [169, 178] were obtained but solvent purity and volatility species are pointed out as significant issues [169].

Takaku *et al.* [170] have determined trace silicon in ultra high purity water for the manufacture of semi-conductors by ICP/MS. A preconcentration procedure was applied, allowing quantification down to sub-ng.L^{-1} of Si. The variation of element concentrations such as B, Si, P and S in steels has a significant influence on the mechanical and physical properties of this material [136]. Thus, Si determination was achieved by ICP/MS [179] or DRC-ICP/QMS [135, 136]. Detection limits varied from 0.2 µg.L^{-1} [135] and 2 µg.L^{-1} [136]

for the introduction of acid solution and precision was better than 6.3% [135]. These LOD are low enough for analysis of nitric acid steel samples [179]. Finally, electrothermal vaporization (ETV) ICP/MS was applied to quantify of silicon trace concentration in solid polyamide samples [180]. According to a comparison between other spectroscopic methods, Resano *et al.* [180] concluded that ETV-ICP/MS and ETAAS have approximately the same performance concerning detection limits in the solid sample (0.3 µg.g^{-1}). De Schrijver *et al.* [181] have showed that the LODs considerably improved with direct solid sampling methods compared to those attainable after dissolution. ICP provides a very sensitive determination of total silicon but these do not provide structural information if it is not coupled to a separation technique (see section 2.6).

2.4.2 NMR methods

NMR has the potential to achieve both total silicon determination and molecular identification [182] mainly in biological fluids and tissues, environmental and petroleum products. The application of three NMR methods (^{1}H-NMR, ^{13}C-NMR and ^{29}Si-NMR) has been widely reported for silicon determination in the Analytical Chemistry of Silicones [183] and in Organosilicon Materials [87]. Varaprath *et al.* [85] have also described numerous works by NMR for the determination of silicon in environmental and biological samples. Nevertheless, ^{29}Si NMR could not detect concentrations below 50 mg.kg^{-1} in these matrices.

In 1990, Fux [184] determined the presence of PDMS in extracts of chemicals after a soxlhet extraction with pentane. A quantification limit of 0.1 mg.kg^{-1} of PDMS was obtained by ^{1}H-NMR. Other works by ^{1}H-NMR and ^{29}Si-NMR for determination of PDMS degradation products in animal models and human tissues have been related [185-187]. Indeed, Garrido *et al.* have shown that silicon migrates from the implant to local and distant sites, and then were located in tissues [185] and blood [186]. The biodegradation of PDMS and D_4 as model compounds in lymph nodes of rats has also been studied by ^{29}Si-NMR [187]. In addition to the resonance associated with the PDMS injected, the NMR spectra showed new resonance, compared with lymph nodes control that are attributed to partially hydrolysed polysiloxanes and silica. Moreover, a critical review article of works by NMR has also reported on this problem as well [188].

The natural abundance of ^{29}Si isotope is only 4.7 % and the NMR signal is weak. However, this technique is attractive for silicon speciation because of the wide distribution of ^{29}Si chemical shifts (120 ppm) from silicon nuclei. In the petroleum domain, Carduner *et al.* [70] determined the presence of Si and identified the chemical nature of the molecules by ^{29}Si-

NMR. Indeed, a resonance was observed at -19.55 ppm that corresponded to octamethylcyclotetrasiloxane (D_4) in unleaded gasoline. Hamilton [182] also reported the detection of PDMS hydrolysis products by ^{29}Si-NMR in the environment. The different chemical shifts were specified for silicon compounds (D_3-D_6, HMDS, DMSD...). D_4 chemical shifts fitted the value reported by Carduner *et al.* [70].

In spite of specified identification of chemical structure and non-destructive technique, NMR is not adapted to trace analysis of several contaminants.[189] Indeed, the ratio of LOD calculated between AAS and ^{29}Si-NMR is approximately 10^4. Carduner *et al.* [70] and Bellama *et al.* [190] also noted that concentrations lower than 60 mg.kg^{-1} of Si in unleaded gasolines and 45 mg.kg^{-1} of Si in environmental samples could not be detected by this technique.

2.4.3 Others methods

Considering the fact that X-Ray fluorescence (XRF) and infra red spectroscopy are not adapted to trace determination of silicon, less attention is paid. However, there were applied in petroleum products, industrial and biological samples with detection limits generally above 10 mg.kg^{-1}. The determination of silicon by XRF [191] and IR [192] was widely reported in The Analytical Chemistry of Silicones. The application of XRF for silicon analysis in heavy oil samples allows quantification with detection limit of 12 mg.kg^{-1} and a reproducibility above 97% [193]. A comparison between XRF and FTIR applied to silicon determination in paper coating has shown that XRF is the more convenient combination between sensitivity and samples preparation [194]. However, FTIR can be possibly used as an alternative of XRF. FTIR has been particularly applied in the determination of silicon in human tissues from breast implant degradation [195-197].

2.5 Silicon contamination and analytical artifacts

As seen in the previous chapters, the important use of silicon compounds in a wide variety of applications (cosmetics, personal care products and consumer goods) increases the potential contamination of samples during the analysis [82, 83]. The purpose of this part is to review the different sources of contamination and the analytical artifacts induced during silicon speciation due to various contamination sources [89]. A relative estimation of silicon contamination based on publication numbers and pollution concentration is illustrated in Figure 2-7. The importance of each source is discussed throughout this chapter. Generally, contamination through human way has to be minimized by taking care of the use of cosmetic and personal care products during Si determination by laboratory personal [89]. Moreover, numerous authors described contamination problems arising from organosiloxanes present in different sources like spare parts made of silicone in various parts of the analyzer or contamination from different sources during sampling and preparation. Thus, extreme care must be taken to minimize the sources of artifacts and siloxane contaminations for speciation analysis at trace levels [198].

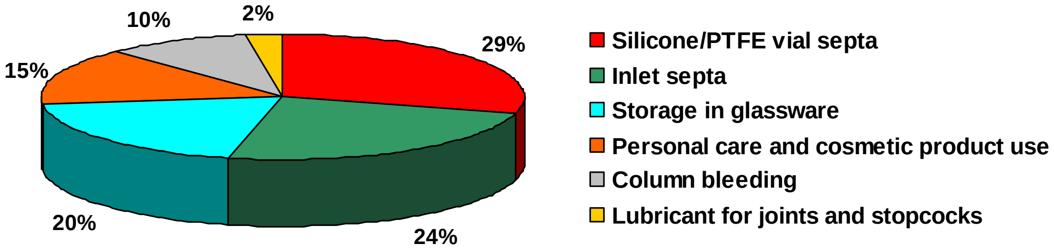


Figure 2-7. Relative estimation of silicon contamination based on literature publications in percent

2.5.1 Contamination in Gas Chromatography

Contamination in GC mainly concerned cyclic siloxanes generated by the inlet septa and column bleeding during analysis. According to Figure 2-7, the degradation influence of the inlet septa is greater than the column bleeding regarding the siloxane levels. Moreover, the contamination augments with the injection temperature. The presence of septa particles located in the liner also contributes to this pollution [199]. Nevertheless, this phenomenon can be reduced by using specific gas chromatography tools.

Septa are made of pure heavily cross-linked PDMS and of phtalates added as stabilizers [199]. At high temperatures (200-300°C), PDMS starts to degrade and produces cyclic siloxanes (D_3-D_{13}) [8, 9, 11] (Figure 2-4). The trimer is reported to be the most abundant product with decreasing amounts of tetramer, pentamer, hexamer and higher oligomers [8]. In order to minimize the impact of septum bleeding, De Zeew recommends several points [199]:

-Avoid the use of a septum and use valve injection such as Merlin Microseal valve [90, 200]

-Reduce the risk of septum scoring by using tapered needles and a prepierced septum (BTO septum)

-Clean the liner (ultrasonic bath) and replace in a time

-Replace the septum frequently

According to this work [199], Horii and Kannan [82] have studied five different septa between 100 and 250°C for injection temperatures. Figure 2-8 shows the D_n concentrations (μg.L^{-1}) as a function of septa used during GC analysis of 1 μL of hexane spiked with an internal standard (M_4Q) at 200°C. The concentrations of D_4, D_5, D_6 measured with an Agilent advanced green septum are respectively 6, 1.6, 4.6 μg.L^{-1} at 250°C and 1.7, 0.6 and 0.3 μg.L^{-1} at 200°C. It corresponds to a drastic reduction (79%) of D_n concentrations. The use of BTO septum at 200°C allows a balance between low levels of D_n and a correct vaporization of compounds (Figure 2-8). Overall, the background of D_6 in blanks is at least 20 times lower than the lowest concentrations found in consumer products [82]. Considering this work, Sparham *et al.* [201] have applied an injection temperature at 150°C to reduce contamination by septum.

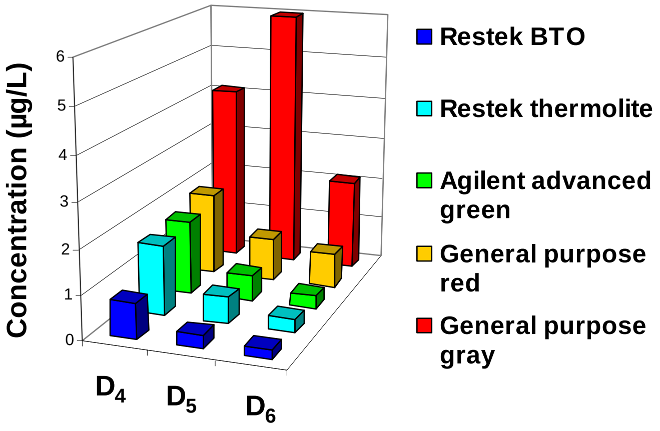


Figure 2-8. Instrumental background levels of D_4, D_5, D_6 in n-hexane injected into several septa of GC/MS at 200°C (Adapted from Horii and Kannan, 2008 [82])

Septum particles can also be deposited in the liner from 200°C to 300°C and caused contamination [85]. One inlet septum particle into the sample extract is almost half of the total amount stationary phase coating of the capillary GC column (a few milligrams for a VF-5 MS) [82, 199]. Consequently, a method is proposed to determine if the septum produces cyclic siloxane compounds based on the simulation of different splitless injection with time variation from 0 to 20 minutes [199].

The generation of these molecules also originated from column bleeding because most of capillary columns are covered with PDMS. Horii *et al.* [82] examined cyclic oligomer backgrounds of two low bleed columns, a DB-5 MS (5% phenyl and 95% PDMS) and a DB-1 MS (100% PDMS). Another column (DB-XLB) has also been studied by Kala *et al.* [118] in 1997 to minimize hexamethylcyclotrisiloxane (D_3) levels in blanks. The results suggested that the release of organosiloxanes from a low bleed column is minor in comparison with the release from septa (Figure 2-7). The fact that D_n contamination mainly originates from septum degradation has been confirmed by De Zeeuw [199] and Wang *et al.* [83]. For example, a DB-5 MS and a DBWAX (phase without silicon) columns produce similar background levels of siloxanes during blank analysis. However, Varaprath *et al.* [202] have also focused their researches on the analytical artifacts related to siloxane analysis. For example, D_4 can be generated by interactions between water contained in biological or environmental samples and PDMS stationary phase in GC. Higher cyclic siloxanes can also be produced at trace levels.

2.5.2 Mass Spectrometry detection and artifacts

In 1982, Ende and Spitleller reported different contaminations in Mass Spectrometry [198]. Several elements present in laboratory (syringe, lubricants, flasks, pump fluids, septa...) contained silicones [85, 198]. For instance, Carter *et al.* [203] suggested that plastic pasteur pipettes contain a silicon lubricant with a molecular weight of approximately 16,500 $g.mol^{-1}$. General precautions to limit contamination are described but even with the highest degree of precaution, these authors suggest that analysts are not able to exclude contamination in trace silicon analysis [198]. Indeed, they can only minimize the risk of contamination.

In association with GC, the degradation products formed by column stationary phase decomposition are similar to the products generated by septa degradation [199]. These compounds induce the formation of artefact ions (m/z 207, m/z 281 and m/z 355) in MS that correspond to major fragment ion of our interest compounds as D_3 ($222\text{-}CH_3$), D_4 ($296\text{-}CH_3$) and D_5 ($370\text{-}CH_3$) [199]. Other ions m/z 73 (Me_3Si^+), m/z 147 $(Me_3SiOSiOMe_2)^+$ m/z 149 (plasticizer), m/z 295 (silicones with M<400) can also appear as contamination sources in the background [85]. Thus, low bleeding and MS quality columns are recommended [199].

2.5.3 Other contaminations, storage and conservation

Several authors have studied the storage and conservation of organosilicon compounds such as silanols and silanediols because of their high reactivity [90]. Sample storage in vial septa made of silicon must be avoided and silicon compounds (DMSD) need storage in plastic containers to eliminate condensation enhanced by alkaline surface.

Various authors focused their works on the contamination induced by the use of silicone/PTFE vial septa [204-206]. Chambers *et al.* [204] and Wang *et al.* [206] demonstrated that silicone/PTFE septa generate D_n compounds when they are in direct contact with the sample. Chambers *et al.* [204] observed the generation of cyclic siloxanes (D_3-D_7) during MTBE (Methyl Tertiary Butyl Ether) analysis in blood at $ng.L^{-1}$ levels by gas chromatography coupled to mass spectrometry (GC/MS) in single ion monitoring mode (SIM). Moreover, the results obtained by Wang *et al.* [206] showed that sample analysis must be made immediately after they are introduced in vials with silicone/PTFE septa in order to avoid the contamination by D_n. On the other hand, Pattinson *et al.* [205] tested nine vial septa with different solvents by GC/MS. They concluded that septa which have a PTFE layer minimize silicon contamination. Thus, vials with butyl/PTFE caps used by Sparham *et al.* [201] have shown a reduction of D_n generation and a minimization of the sample volatilization more observed with PTFE septa.

Storage and conservation play an important role during trace analysis. Silicon materials, such as PDMS, have a great affinity for glass and are often adsorbed on the surface [86]. Thus, it is more safe to keep them at lower temperatures in teflon or plastic containers (preferentially high density polyethylene) [85]. This precaution is particularly true for silanols that condense and siloxanes that react in the presence of alkaline surface, acids or strong bases [86]. Indeed, glass surfaces, moisture, temperature and acidity will improve condensation [90]. Several authors [82, 99, 207] suggest to store samples in polypropylene vials before their analysis.

Varaprath and Lehmann [90] have also studied the conservation and stability of the dimethylsilanediol (DMSD) by ^{29}Si NMR and HPLC (high pressure liquid chromatography) at different concentrations. This compound is unstable even in pure form [208] and must be stored in a freezer between 4 and 8 weeks in plastic container with a drying agent in order to avoid polymerization and the presence of dimerdiol at high concentration [90]. At a lower concentration (100 mg.L^{-1}), HPLC results confirmed that DMSD is stable during one year.

2.6 Hyphenated techniques for Silicon speciation

Several hyphenated techniques have been developed for Si speciation using chromatographic methods (Figure 2-6). These separation techniques are based on different physico-chemical properties, such as volatility, molecular size, degree of aromaticity or polarity. This chapter is mainly focused on the combination of chromatographic methods (LC, GC and SFC) with different detectors reported in Figure 2-6. However, other techniques such as mass spectrometry have been employed for Si speciation.

2.6.1 Liquid chromatography

For silicon speciation, LC has been employed in two separation techniques: high pressure liquid chromatography (HPLC) for LMW compounds and size exclusion chromatography

(SEC) for HMW molecules (Figure 2-6). HPLC can be performed in normal phase (NP) or reverse phase (RP). Basically and for silicon speciation, applications by NP-HPLC are smaller than RP-HPLC.

2.6.1.1 High Pressure Liquid Chromatography (HPLC)

HPLC analysis enables the separation of polar and non polar compounds that do not elute under normal GC analysis conditions such as low volatile, highly polar or thermally unstable molecules [85]. For silicon speciation, reversed-phase HPLC is carried out using a C_{18} (octadecylsilica) stationary phase and elution with a polar solvent (methanol, acetonitrile, water).

Several researchers have employed RP-HPLC for LMW silicon molecules in environmental and biological samples using classical detectors (UV, RI, radioisotope) [209, 210] or ^{29}Si NMR [211] to provide molecular identification. However, most of the works have been performed by the coupling of RP-HPLC and atomic detectors (ICP-OES and ICP/MS) allowing structural information with the LC separation and selectivity detection [99, 203, 207, 212-215] (Figure 2-6). Generally, a considerable improvement of LOD is observed when ICP-OES (20-500 µg.L^{-1}) is replaced by ICP/MS detection (0.1-4 µg.L^{-1}). However, according to Ebdon *et al.* [215], ICP-OES is a more attractive detector for silicon speciation when compared to ICP/MS because mass interferences (m/z 28) are deleted. RP-HPLC analyses for Si speciation are summarized in Table 2-2.

Table 2-2. HPLC methods for silicon speciation

Matrices	Molecules	Solvent	Injection volume (µL)	Column	Mobile Phase	Flow rate (mL.min^{-1})	Detection	LOD	Ref.
Soil	Dimethylsilanediol	THF	—	C18 25cmx4.6mmx5µm	H_2O (100) H_2O (100) to ACN (100) ACN (100) to H_2O (100)	—	Refractive index	—	[90]
Biogas	Inorganic silicon Dimethylsilanediol 1,3-tetramethylsilanediol Trimethylsilanol	H_2O	100	C18 25cmx2mm	ACN/H_2O (20/80) ACN/H_2O (5/95) ACN/H_2O (60/40) for Flushing	0.3	ICP-OES	500 µg.L^{-1} of Si 30 µg.L^{-1} of Si	[99]
Environmental	Methylsilanediols	Xylene	25	C18 25cmx2mm	ACN/H_2O (1:10) to ACN/H_2O (4:10)	0.2	ICP-OES	40-150 µg.L^{-1} of Si	[207]
Biological	L_2 D_5 and its metabolites	mobile phase	—	C18 25cmx4.6mmx5µm	H_2O (100) H_2O (100) to ACN (100) ACN (100) ACN (100) to H_2O (100)	—	Radioisotope	—	[210]
	D_4 and its metabolites	mobile phase	—	C18 25cmx4.6mmx5µm	H_2O (100) H_2O (100) to ACN (100) ACN (100) to H_2O (100)	—	Radioisotope Refractive index	—	[209]
Medical	Inorganic silicon 1,3-tetramethylsilanediol L_2	mobile phase	100	C18 25cmx2mm	MeOH/H_2O (30/70)	1	ICP-OES	100 µg.L^{-1} of Si 400 500	[215]
	Inorganic silicon Dimethylsilandiol 1,3-tetramethylsilanediol	mobile phase	100	C18 25cmx2.5mmx6µm	MeOH/H_2O (20/80)	0.15	ICP/MS	0,1 µg.L^{-1} of Si 4 4	[203]
Polymer	L_2-L_5, D_3-D_5	AcOEt	5	C18 15cmx4.6mmx5µm	MeOH/H_2O (95/5) to MeOH (100)	1	ICP-OES	20-50 µg.L^{-1} of Si	[212]
	L_2 PDMS	Acetone	5	Carbosphere 30 DS	ACN/Acetone (80/20) 30-130°C at 2°C/min 130°C (8 min)	0.20	ICP-OES	40 µg.L^{-1} of Si	[213]
	Hexamethydisilane L_3 and L_5 PDMS	ACN $CDCl_3$	60	C18 15cmx4.6mmx5µm	ACN/$CDCl_3$: (9:1) to ACN/$CDCl_3$ (1:9)	0.5	^{1}H NMR ^{29}Si NMR	—	[211]
Organic matrices	D_4	Xylene Hexane	—	C18 30cmx10µm	MeOH/H_2O (7:10) to MeOH(10)	1	ICP-OES	500 µg.L^{-1} of Si	[214]

Varaprath *et al.* [210] detected several metabolites of hexamethyldisiloxane (L_2) and decamethylcyclopentasiloxane (D_5) and also metabolites of D_4 [209] in animal urine by RP-HPLC with a radioisotope detection. Metabolites were eluted on a C_{18} column using a ACN/H_2O mobile phase. The main structures were confirmed by synthesizing ^{14}C-labeled standards and GC/MS was applied in order to further confirm their identities [209, 210]. DMSD was detected by refractive index detector during PDMS degradation in soils [90, 216]. These previous detectors provide a non-destructive technique but without the sensitivity to allow trace analysis [85].

As previously mentioned, Si speciation in the environment by RP-HPLC-ICP-OES has been reported (Figure 2-2). Firstly, the detection and the linearity response of D_4 in xylene and hexane matrices have been achieved with detection limits of 500 $\mu g.L^{-1}$ [214]. Similarly, Biggs *et al.* [212] carried out silicon molecules separation (L_2-L_5 and D_3-D_5) with improved LODs ranging from 20 and 50 $\mu g.L^{-1}$ of Si with this combination. According to gradient and column optimization, elution on a C_{18} column (15cmx4.6mmx5µm) with a gradient from MeOH/H_2O (90/10) to MeOH (100) over 8 minutes produces the best results [212]. Nevertheless, chromatographic separation observed respectively between D_4 and L_3 and between D_5 and L_4 is not optimal. The same authors have also indicated the improvement of thermal gradient by RP-HPLC-ICP-OES for PDMS solution in acetone with a ACN/Acetone gradient [213].

In 1994, the speciation of silanediols in water, sludge extracts and soils was carried out by RP-HPLC-ICP-OES with detection limits of 40 $\mu g.L^{-1}$ of Si for trimerdiol and 150 $\mu g.L^{-1}$ of Si for monomer and dimerdiol [207]. It was also shown that low injection volume and use of xylene minimize the instability of the plasma to organic solvents. Grumping and Hirner [99] performed the separation of two silanediols and trimethylsilanol (TMS) in leachate samples by the same hyphenated technique. Detection limits of 30 $\mu g.L^{-1}$ of Si for TMS and 500 $\mu g.L^{-1}$ of Si for DMSD were calculated for 100 µL injection volume. Additionally, a modification of eluent by a more polar gradient allowed the separation of the DMSD and the silicate [99] (Table 2-2). Dorn and Kelly [207] obtained DMSD lower detection limits than Grumping and Hirner [99] because of the different gradient application and the use of a special ICP interface and micro HPLC system.

More recently, Ebdon *et al.* [215] compared the performance of RP-HPLC with a radial ICP and an axial ICP for polar silicon compounds. Generally, it is well known that detection limits are improved using axial ICP compared to radial ICP [217]. However, radially viewed ICP-

OES gave similar detection limits (100, 400 and 500 µg.L^{-1} of Si for inorganic silicon, TMSD and L_2 respectively) to axially viewed ICP-OES with improved chromatographic peak reproducibility for all three compounds [215]. In 2004, Carter *et al.* [203] replaced the ICP-OES with ICP/HRMS coupled to RP-HPLC for Si speciation. Consequently, using similar conditions to previous study [215], an improvement of detection limits for inorganic silicon compound with a 1:1000 ratio and for TMSD with a 1:100 ratio was indicated [203] (Table 2-2). These results show that ICP/MS provides better detection limits than ICP-OES for Si speciation when mass interferences are resolved. Finally, reversed-phase LC-NMR with ^1H and ^{29}Si has been developed using a gradient from ACN/$CDCl_3$ (9:1) to ACN/$CDCl_3$ (1:9) in order to determine several organosiloxane structures [211].

2.6.1.2 Size Exclusion Chromatography (SEC)

This technique, also referred to as gel permeation chromatography (GPC) is commonly used for unravelling HMW molecule behaviour in environmental, biological tissues and industrial applications [218]. SEC separates molecules on the basis of their size, or more precisely on their hydrodynamic volume. It is employed in silicon speciation for PDMS degradation in environmental conditions by using SEC with a refractive index detector [96, 109] or an ICP technique with detection limits reported below sub-mg.kg^{-1} [110, 219]. Several researchers have also combined SEC and mass spectrometry for identification of silicon polymers.

Hausler and Taylor have achieved PDMS separation by SEC-ICP-OES with detection limits ranging between 0.03 to 3 mg.L^{-1} of Si [220, 221]. This hyphenated technique was applied in water and sludge extracts with LOD of 160 µg.L^{-1} of Si [207]. PDMS separation with molecular mass between 550 and 500,000 g.mol^{-1} using THF and xylene as mobile phases has been established. Xylene was chosen because it enables to easily maintain a stable plasma and allows the solubilisation of most of the PDMS polymers. Nevertheless, using THF iso-response as a function of molecular mass and upgrade in sensitivity by a factor 4 are observed. This is due to the better solubility of PDMS polymer in THF, particularly for high weight mass polymer [207].

Carter *et al.* [203] reported a similar separation of three PDMS polymers (162, 1500 and 16,500 g.mol^{-1}) by SEC-ICP/MS with detection limits of 12, 26 and 30 µg.L^{-1} of Si respectively. Extraction efficiencies of these compounds from spiked human plasma were performed with xylene because of its relatively low vapour pressure (plasma stability [207]) and compatibility as an elution solvent for the SEC separation [203].

Maziar *et al.* [222] have studied HB-PDMS (α,w-bis(4-hydroxybutyl) polydimethysiloxane) behaviour by SEC-MALDI/TOFMS in order to obtain detailed information during synthesis. A comparative study between automated SEC-MALDI/TOFMS and on-line SEC-ESI/TOFMS for PDMS characterization demonstrated an improvement of chromatographic resolution and an enhancement in low molecular weight polymer ($M<550\ g.mol^{-1}$) by this latter coupling [223]. In opposition, the first technique effectively reported the HMW oligomers and underestimated the LMW oligomers [223].

2.6.2 Gas chromatography

Gas chromatography has been widely used for Si speciation (Figure 2-2). An enhancement in separation compared to HPLC based on the volatility and the polarity of species can be achieved by GC. Figure 2-6 summarizes various detectors for silicon reported in the literature. GC is preferred to LC because of higher resolution and lower detection limits. For instance, chromatographic resolution between silicon molecules like D_4 and L_3 is better by GC-ICP-OES [99] than by LC-ICP-OES [224]. GC chromatography applied for Si speciation in environmental (Table 2-3), biological and industrial samples (Table 2-4) are presented. Most of the studies is carried out on non polar columns (95% methylPolysiloxanes-5% Phenyl) with 1µL injection volume in splitless mode.

Table 2-3. Gas Chromatography methods for silicon speciation in environmental samples

Matrices	Molecules	Solvent	Injection	Column	Detection	LOD; Si Eq.*	Ref.
Soil	D_4-D_6 Silanediols (1-5)	THF Acetone	1 µL 250°C	HP5 30mx0.25mmx0.25µm	MS SIM	1 µg.L^{-1}; 0.4 µg.L^{-1} of Si 0.1-1 mg.L^{-1}; 0.04-0.4 mg.L^{-1} of Si	[90]
	Silicon degradation products	THF Acetone Hexane	Merlin System 2µL 250°C	HP5 30mx0.25mmx0.25µm	MS Full Scan	—	[200]
	Dimethylsilanediol	THF	1µL 250°C	HP5 30mx0.25mmx0.25µm	MS SIM	—	[101]
	Dimethylsilanediol silanols D_n	THF Acetone	2µL 250°C	DB1 60mx0.32mmx0.25µm	MS SIM	—	[103]
Water	D_5	Hexane	3 ml in HS 220°C	DB-FFAP 30mx0.25mmx0.25µm	MS SIM	3 ng.L^{-1}; 1.1 ng.L^{-1} of Si	[201]
Air	D_3-D_5	—	—	HP5-MS 30mx0.25mmx0.25µm	MS SIM	—	[225]
	D_3-D_4 L_5 Tetramethylsilane	—	180°C	200 f t OV-17 200 ft OV-101 400ft OV-101	MS Full Scan	—	[226]
	Alkoxysilanes	Heptane	1 µL	DB5 30mx0.32mmx0.25µm	FID	1-5 mg.L^{-1}; 0.12-0.62 mg.L^{-1} of Si	[123]
Air, Water, Soil, Sediments, Biota	D_3 D_4-D_6 L_2-L_5	Hexane	1 µL 200°C	CP-Sil8CB 30mx0.25mmx0.5µm	MS SIM	50 µg.L^{-1}; 18.9 µg.L^{-1} of Si 5 µg.L^{-1}; 1.9 µg.L^{-1} of Si 0.3-0.5 µg.L^{-1}; 0.11-0.18 µg.L^{-1} of Si	[78]
Biogas	L_2-L_4, D_3-D_6 et Trimethylsilanol	Pentane	200°C	RTx-1 47 mx0.32mmx1.5µm	AED MS Full Scan	9.5 µg.L^{-1} of Si —	[100]
Waste Sludge	L_2 et D_3-D_6	Hexane	1 µL 125°C	VF-1MS	FID	—	[97]
Waste	D_3-D_5; L_2-L_4 Trimethylsilanol	pentane	5 µL	HP1	ICP-OES	0.1 µg.L^{-1} of Si** —	[224]
	D_3-D_6	Hexane	1µL 240°C	SE-54 50mx0.32mmx0.25µm	FID MS Full Scan	—	[98]

*Si Eq.: Silicon Equivalent; ** Estimated

Table 2-4. Gas Chromatography methods for silicon speciation in biological and industrial samples

Matrices	Molecules	Solvent	Injection	Column	Detection	LOD; Si Eq. *	Ref.
Biological	D_4	Tetrahydrofuran	Merlin System 2µL 250°C	HP5-MS 30mx0.25mmx0.25µm	MS SIM	1 µg.L^{-1}; 0.4 µg.L^{-1} of Si	[202]
Blood, Plasma	D_3-D_6	Hexane	— 200°C	HP5 30mx0.25mmx0.25µm	MS SIM	2 µg.L^{-1}; 0.76 µg.L^{-1} of Si	[117]
	D_4	Tetrahydrofuran	2µL 250°C	ND5-MS 30mx0.25mmx0.25µm	MS SIM	4.9 µg.kg^{-1}; 1.9 µg.kg^{-1} of Si	[81]
Tissues	D_3-D_6	Hexane	— 200°C	HP5 30mx0.25mmx0.25µm	MS SIM	—	[119]
Breast Implants	PDMS D_n	Ethyl Acetate	1 µL 320°C	DB1-HT 30mx0.32 mmx0.2 µm	AED MS SIM	80 µg.L^{-1} of Si 100 µg.kg^{-1}; 38 µg.kg^{-1} of Si	[120]
	D_n and L_n	Ethyl Acetate	—	Extra Low bleed DR-XLE	MS SIM AED	— —	[118]
Medical	silylated alcool	Pyridine	1 µL	FS-Suprem-5 25mx0.25mmx0.25µm	ICP/MS	3 µg.L^{-1} of Si **	[227]
Consumption products	D_4-D_7 L_5-L_{14}	Ethyl Acetate Hexane	1 µL 200°C	Rxi5-MS 30mx0.25mmx0.25µm	MS SIM	117 µg.kg^{-1}; 44 µg.kg^{-1} of Si 18 µg.kg^{-1}; 6.8 µg.kg^{-1} of Si	[82]
	D_3 D_4-D_6	Methanol Acetone Hexane	280°C	DB5-MS 30mx0,25mmx0,25 µm	MS SIM	120 µg.kg^{-1}; 45.3 µg.kg^{-1} of Si 80 µg.kg^{-1}; 30.2 µg.kg^{-1} of Si	[83]
Polymer	D_3-D_8	Toluène	1µL 250°C	MDN-5S 30mx0.25mmx0.25µm	MS Full Scan	—	[228]
	D_n et L_n	Dichloromethane Chloroform	200°C	DB5 30mx0.25mmx0.25µm	MS Full Scan	—	[229]
	D_3-D_{10}	—	—	CP-Sil 8 30mx0.25mmx0.25µm	MS Full Scan	—	[230]
	degradation resin products	Tricholormethane	250°C	Anabond 225 50mx0.32mmx1µm	MS Full Scan	—	[231]
	D_3-D_6	—	200°C	100% methylsilicone	MS Full Scan	—	[232]

*Si Eq.: Silicon Equivalent; ** Estimated

2.6.2.1 GC-FID

This coupling was mainly used during workers exposure in the silicon industry and in biogas samples but it is not very adapted to trace analysis due to poor detection limits. Firstly, three alkoxysilanes have been detected by GC-FID using heptane as dilution solvent with detection limits ranging from 1 to 5 $mg.L^{-1}$ in order to carry out worker exposure to silicon compounds [123]. More recently, the determination of cyclic siloxanes (D_3-D_6) in waste samples has been performed by GC-FID after a successful extraction by XAD-2 resins using hexane [98]. Note that the identification is possible by matching the retention time with analytical standards. However, completed identification was achieved by GC/MS [98]. After a liquid-liquid extraction with hexane, Dewil *et al.* [97] have separated D_4 and D_5 by GC-FID on a non-polar column in waste sludge. Excellent correlation coefficients ($R^2>0.999$) were obtained up to 1000 $mg.L^{-1}$. Popat *et al.* [233] have also identified D_4 in biogas with detection limits of 1 $mg.m^{-3}$.

2.6.2.2 GC/MS

According to Figure 2-2, GC/MS is the most hyphenated technique employed for Si speciation in environmental, biological and industrial matrices. Mass spectrometry (MS) detection can be mainly performed in full scan (FS) mode especially for qualitative analysis and in SIM (Selected Ion Monitoring) mode for trace quantitative measurement (Table 2-3 and Table 2-4). GC/MS is one of the most sensitive technique when it is carried out using the latter mode [85] with detection limits generally ranged between 1 and 100 $\mu g.kg^{-1}$. Reactive polar compounds such as silanols and silanediols caused analysis problem which could be solved by CI use or derivatization procedures.

D_n (D_4-D_6) and silanediols (mono-pentamer) were extracted from soils with polar solvent (THF, acetone) and identified using SIM mode *via* two ionization methods [90]. Detection limits of 1 $\mu g.L^{-1}$ with a signal to noise ratio of 5 for D_n and between 100 $\mu g.L^{-1}$ and 1 $mg.L^{-1}$ for diols have been calculated. In order to differentiate these compounds which have the same fragmentation patterns in their mass spectrum, some authors [90, 229] have preferred to work using chemical ionization (CI) instead of electron impact ionization (EI).

Siloxanes lose a methyl group (M-15) under EI conditions. On the other hand, silanediols (excepted DMSD and Dimerdiol) lose a water molecule (18) in addition to a methyl group (M-33), trimer, tetramer and pentamer diols have a mass difference of 18 with D_3, D_4, D_5 respectively. Thus, their mass spectrum is similar (M-15) [90]. Although these compounds can be distinguished by their retention time in GC, CI helps to identify these molecules. For instance, the identification of D_4 (m/z 314) and tetramerdiol (m/z 332) with a mixture of reagent gas CH_4:NH_3 (90:10) $[M+NH_4]^+$ [90] and D_n compounds using isobutane $[M+H]^+$ [229] were carried out.

Other VMS (D_3-D_5, L_5 and tetramethylsilane) were detected by GC/MS in ambient atmospheric extracts [225, 226]. More recently, D_5 analysis was performed in river water and treated waste water by hexane extraction and head space (HS) coupled to GC/MS SIM using a DB-FFAP column [201]. The use of internal standard in SIM mode (m/z 73, m/z 267, m/z 355 for D_5 and m/z 360 for $^{13}C_5$-D_5) provides a quantification limit of 10 ng.L^{-1} for D_5 in water. In 2005, concentrations of cyclic and linear oligomers were reported by GC/MS SIM in the nordic environment (water, sediments, air, sludge, biota...) of six countries [78]. Detection limits have been calculated for various matrices after an hexane extraction. For instance, detection limits for D_3, D_4-D_6 and L_2-L_5 were found to be 50, 5 and between 0.3 and 0.5 µg.kg^{-1} in biota samples respectively.

Analysis of polar silicon compounds, such as silanols or silanediols may require derivatization by sylilating agents before GC analysis due to their instability (see chapter 3) [85, 90]. Basically, if stationary phase contents siloxanes, the formation of reactive hydrogen atoms can appear in presence of moisture [85] and promotes silanol condensation into the GC column [234]. Consequently, this reaction compromises severely the sensitivity and degenerates the peak shapes [90]. Several workers have capped OH functions of the molecules with trimethylsilyl groups [234], by usually using BSTFA (bis(trimethylsilyl)-trifluoroacetamide) [200]. However, Varaprath *et al.* [90] have shown that species like DMSD can be analyzed without derivatization reaction. The procedure described a 1µL BSA (bis(trimethylsilyl)acetamide) injection volume into GC column before analysis in order to deplete all reactive surfaces [90]. In opposition, Lehmann *et al.* [101, 103] have achieved the direct detection of DMSD, silanols and D_n without derivatization step by GC/MS SIM during PDMS degradation in soil .

Cyclic and linear compounds were also analyzed by GC/MS in FS mode for qualitative analysis and in SIM mode for quantitative study in biological matrices. After extraction by ethyl acetate and THF, detection limits of 100 µg.kg^{-1} for tissue [120] and 5 µg.kg^{-1} [81] in plasma samples have been respectively reported by SIM mode. Several workers quantified D_n in blood and plasma using a widely internal standard M_4Q (tetrakis(trimethylsiloxy)silane) for Si speciation [81, 82, 117, 202]. Extraction yields above 90% with THF and a 2µL injection volume gave access to very low detection limits around 1 µg.L^{-1} [202]. In addition, linearity range between 1 to 16 µg.L^{-1} of D_4 compared to internal standard was obtained. Considering the same analytical method, Flassbeck *et al.* [117] calculated detection limits of 2 µg.L^{-1} after an hexane extraction of D_n from blood and plasma, which is similar to the values reported in the literature [81, 90, 202].

As previously mentioned in section 2.2, silicon molecules are used in consumer products. Horii and Kannan [82] measured high VMS (D_n and L_n) levels in 76 cosmetic and personal care products by SIM mode. After an extraction by a mixture of ethyl acetate/hexane, 1µL of analyte injected in a Rxi-5 MS column at 200°C has allowed the acquisition of detection limits ranging between 18 (L_n) and 120 µg.kg^{-1} (D_n). Details in contamination problems were also given (see section 2.5 for more details) [82]. More recently, cVMS have been analyzed in 252 consumer products by GC/MS (fragrances, hair care products, antiperspirants, lotions...) [83] using similar conditions to Horii and Kannan [82]. Detection limits between 120 µg.kg^{-1} (D_3) and 80 µg.kg^{-1} (D_4-D_6) and calibration curve ranging from 50 µg.kg^{-1} to 10 mg.kg^{-1} were reported [83]. According to a comparison between D_5 and D_6 levels in skin lotions achieved by Horii and Kannan [82] (35.3 mg.g^{-1} and 6.3 mg.g^{-1}) and by Wang *et al.* [83] (47.3 mg.g^{-1} and 6.5 mg.g^{-1}), these studies are completely in agreement.

GC/MS has also been applied for Si speciation mainly in FS mode for qualitative analysis. Silicon compounds (siloxanes and chlorosilanes) were separated by GC and identified by MS in EI and in CI for silicon rubber and silicon resins respectively [231, 232]. Furthermore, D_n characterization was performed by GC/MS when PDMS was submitted to corona discharges [230]. Wacholz *et al.* [229] have also analyzed a mixture of cyclic and linear siloxanes by GC/MS and GC-FTIR. More recently, thermal stability of polysiloxanes has been studied by HS-GC/MS in toluene [228]. These results have shown the presence of D_n, phtalates and ethylhexanoic acid. In addition, Hall *et al.* [228] have reported a non-linear response for D_5 and L_5 contrary to Sparham *et al.* [201] researches.

2.6.2.3 GC with atomic detection

Contrary to GC/MS when it performed in SIM mode, the combination between GC and atomic detector such as AED, ICP-OES and ICP/MS are relatively scarce even if providing sub µg.L^{-1} detection limits and structural information (Figure 2-2). According to our own knowledge, GC-AED is the most reported coupling with atomic detection [100, 118, 120] and only two papers have been published in Si speciation by GC-ICP-OES in biogas [224] and by GC-ICP/MS in medical field [227]. However, this hyphenation, mainly GC-ICP/HRMS appears as a versatile analytical tool for silicon speciation. Indeed, the high resolving capacity of GC and the high sensitivity, selectivity and multi-elements of ICP/MS have made the combination more efficient and attractive for speciation analysis of different elements in complex matrices, such as environmental, biological and petroleum and derived products [235-238]. For silicon speciation, only one application of GC-ICP/MS was carried out for silylated alcohol standard solutions in medical field [227] and its use has never been extended to real matrices.

In 1997, a novel and highly sensitive method for detection, quantification and characterization of LMW siloxanes in biological tissues by GC-AED and GC/MS for further identification has been reported [120]. After an extraction by ethyl acetate, detection limit of 100 µg of Si per kg of tissue was calculated by GC-AED at 251.6 nm using a DB-1 column. Similarly, Lykissa *et al.* [118] identified cyclic compounds (D_3-D_7) and L_7 in silicon gels implants with extra low bleed column in order to minimize Si contamination (see section 2.5).

The development of canister sampling and GC/MS-AED was performed by Schweigkofler and Niessner [100] for the determination of siloxanes (D_n and L_n) and silanols. Detector signals obtained are linear over more than 4 orders of magnitude ($R^2>0.99$) and detection limit of 9.5 µg.L^{-1} of Si was determined in pentane. After thermodesorption and analysis, L_2-L_4, D_3-D_6 and TMS are the major compounds found in biogas with detection limits of 342 ng.m^{-3} [100]. As mentioned in section 2.3, LOD depend on sample extraction and concentration before analysis. Consequently, the comparison of sensitivity between two different techniques is accurate in biogas analysis especially considering collected sampling volume.

Grumping *et al.* [224] identified TMS, L_2 and cyclic oligomers (D_3-D_5) in biogas sample by LT-GC-ICP-OES. For example, VMS (L_2, D_3-D_5) were measured at concentrations ranging between 0.1 and 1.1 µg of Si.L^{-1} of waste water samples. In addition, resolution between L_2 and TMS was non-optimal using a non-polar column (100% PDMS). Different responses between compounds of interest have also been observed due to molecule volatility or condensation phenomena [224]. According to Grumping *et al.* [224], the choice of ICP-OES avoids mass interferences (m/z 28) occurring in ICP/MS when collision/reaction chamber is not available (previously mentioned in section 2.4.1.3). The second study concerns the application of GC-ICP/HRMS to silylated alcohols quantification [227]. Sylilation was achieved by reaction between four alcohols (C_4-C_7) with N-methyl-N-trimethylsilyltrifluoracetamide (MSTFA) in pyridine. Medium resolution (m/Δm=4000) gives access to the resolving of mass interferences between $^{28}Si^+$, $^{12}C^{16}O^+$ and $^{14}N_2^+$ [170, 203, 227] in order to obtain detection limits of 0.1 µmol.L^{-1}, which correspond to 3 µg.L^{-1} of Si for C_4 silylated alcohol [227]. Nevertheless, column bleeding can limit these detection limits and contribute to the background pollution [227].

2.6.3 Supercritical Fluid Chromatography (SFC)

Silicon is dispersed in very low levels for several fields such as environment [90] biology [117] and petroleum and derived products [16, 129]. SFC method is not very adapted to trace analysis and the combination between SFC and detector like ICP-OES, FID or MS don't lead to sufficient sensitivity. Indeed, SFC coupled to an atomic detector (ICP-OES) was achieved to separate various siloxanes with detection limits of 57.9 mg.kg^{-1} for Si [239]. Excellent separation of PDMS with a molecular mass of 2000 g.mol^{-1} has been reported by SFC-FID [240]. This method was applied with SFC/MS for the determination and the identification of cyclic siloxanes in technical silicon oils and rubbers [241].

2.6.4 Other Mass Spectrometry techniques

Without chromatographic separation, mass spectrometry avoids contamination due to the GC part (see section 2.5) and is applied both for LMW and HMW silicon molecules (Figure 2-6). These techniques were mainly performed in environment (soil [242] and biogas [243, 244]) with variable sensitivity depending on the sample preparation (2 µg.m^{-3} [244] and 50 mg.kg^{-1} [242]) and in polymer characterization (FT-ICR/MS and TOFMS) usually as qualitative analysis for industrial applications.

The determination of D_4 and D_5 in biogas by APCI/MS/MS without extraction or prior chromatographic separation was a primer in Si speciation [243]. Badjagbo *et al.* [243] developed and validated a sensitive ($4<\text{LOD}$ (µg.m^{-3}of air)<6) and selective method for direct analysis of siloxanes in gaseous matrices. Indeed, direct MS detection completely avoided background contamination from GC systems (section 2.6) and allows the direct distinction between VMS and siloxanediols previously discussed (section 2.6.2.2) due to the soft APCI ionization $[M+H]^+$ [243]. More recently, Badjagbo *et al.* [244] quantified D_4 and D_5 with an internal deuterated standard hexamethyldisiloxane (HMDS-*d18*) using the previous analytical method [243]. The use of HMDS-*d18* provided effective signal compensation of D_4 and D_5 and improved the sensitivity and reliability of these compounds in biogas [244]. According to Badjagbo *et al.* [244], detection limit around 2 µg.m^{-3} was obtained, which are 500 times better than that reported for a GC-FID [233] and much more sensitive than that reported in a recent study by a microcantilever array sensor. The latter method, recently developed by Long *et al.* [113], provided linear and cyclic siloxanes analysis in biogas with detection limits of 17 µg.L^{-1} for D_5, corresponding to 257 µg.m^{-3} [113]. After possible adsorption or deposition of silicon in the environment (section 2.2.2), a method for isotopic determination of ^{30}Si by MS in plants and soils was proposed with detection limits of 50 mg.kg^{-1} for the soil samples [242]. MS is applied to have a better control of silicon compounds present in industrial applications such as semiconductor and packaging industries [245] and also in some processes [246]. For instance, in-situ MS was carried out to characterize silicon compounds (tetraethoxysilane and hexamethyldisiloxane) enabling the production of protective layers for semiconductors [245]. In addition, Apicella *et al*. [246] observed siloxane series after an extraction by dichloromethane during the analysis of soot recovered in fuel-rich flames using several burners and different fuels by MALDI/MS. In addition, Apicella *et al.* [246] observed siloxane series after an extraction by dichloromethane during the analysis of soot formed in fuel-rich flames by MALDI/MS.

For HMW silicon compounds (Figure 2-6) that do not elute in GC, mass spectrometry methods without separation such as MALDI/TOFMS (time of flight mass spectrometry) or ESI-FT-ICR/MS (Fourier transform-ion cyclotron resonance mass spectrometry) was applied to silicon molecules [85]. In polymer synthesis, the degree of intramolecular condensation, defined as the number of residual silanol (Si-OH) groups per oligomer, for a variety of silsesquioxane polymer (thermal stability and chemical resistance), was measured by MALDI/TOFMS [247, 248]. Indeed, condensation of the Si-OH groups leads to the formation of intramolecular group Si-O-Si bridges accompanied by the loss of water [248]. This phenomenon was easily characterized by high resolution MS [247]. The use of high resolution MS, like FT-ICR/MS [249] offers a sub-ppm mass measurement accuracy and allows successful identification of polymers which generally provide nearly identical mass spectra at low m/z [250]. Murthy *et al.* [251] studied the kinetics and pathways of the ion-molecule reactions for a mixture of silanes and chlorosilanes (SiH_nCl_{4-n}) by FT-ICR/MS using a 1 Tesla magnet and EI ionization. By coupling Electrospray ionization (ESI) to FT-ICR/MS, the first work on PDMS pointed out several fragmentation patterns by hydrogen bond rupture or by methyl transfer [250]. Another study by ESI-FT-ICR/MS in positive ion mode demonstrated the benefit of high resolution in order to characterize resulting molecules, but also to determine fragmentation pathways [252]. Note that polymer containing labile hydrogen in terminal groups can easily undergo a fragmentation in gas phase and generated species with silanol groups [252]. Tecklenburg *et al.* [253] compared ESI-FT-ICR/MS and MALDI/MS for the characterization of silsesquioxane polymers. Samples are prepared in a mixture chloroform/methanol with addition of ammonium acetate to improve silicone ionization. Mass accuracy down to 5 ppm was reported for each fraction and Si isotopes (^{28}Si, ^{29}Si and ^{30}Si) were identified in one structure [253]. In conclusion, MS methods with or without chromatographic separation allow identification and quantitative analysis of Si compounds.

2.7 Conclusions

Due to their wide use in many applications, silicones are spread in several matrices, mainly in environmental and biological, usually at trace concentrations where they have negative impacts. Many analytical methods improve the identification of silicon compounds in environmental, biological and industrial fields. Two different analytical strategies were investigated for silicon analysis: direct methods for total silicon determination and hyphenated techniques for silicon speciation.

However, the unravelling of silicon speciation is relatively scarce, particularly in petroleum and derived samples where complex reactions can occur. Indeed, the matrix complexity associated to contamination, instability and trace level presence makes silicon analysis very hard to achieve. Besides, contamination must be minimized using analyzer specific parts and with care concerning sample conservation and storage.

Atomic spectroscopic methods were usually employed for total Si determination. AAS is one of the first technique used for Si determination with detection limits near equal to 1 mg.L^{-1} for environmental and biological samples. The application of ICP-OES and ICP/MS in environmental, biological and industrial matrices progressed over the decades due to their sensitivity (sub µg.L^{-1} and sub ng.L^{-1} respectively), selectivity and robustness performance. Nevertheless, these analytical methods do not allow molecular separation and identification (speciation) unless there are not coupled to a separation technique. On the opposite, NMR methods have the potential to achieve silicon determination but also silicon speciation at high levels (50 mg.kg^{-1}) in various matrices.

Hyphenated techniques based on the coupling of a chromatographic separation (GC, LC) giving access to retention time, and a sensitive detection (SIM, AED, ICP) are an established versatile analytical tool for Si speciation. GC/MS in SIM mode has proved to be very effective for silicon speciation with detection levels of nearly 1 µg.kg^{-1} although possible contamination can occur by column and septum bleeding. MS detection (MS/MS, FT-ICR/MS) without previous separation avoids contamination by GC parts and offers bright perspectives both for LMW and HMW molecules respectively in environmental and polymer field respectively. The coupling between SEC and appropriate detection also allows a better understanding of HMW silicon molecules. RP-HPLC-ICP appears as a good alternative for sensitivity with detection limits ranging between 0.1 and 500 µg.L^{-1} for LMW molecules in environmental and biological samples but chromatographic resolution is lower than GC. Thus, GC separation combined to atomic detectors such as AED, ICP-OES and ICP/MS seems to be the more convenient solution with LOD ranging between 0.1 and 10 µg.L^{-1} for Si speciation.

Considering that detection limits greatly depend on sample extraction and concentration, sensitivity comparison is a hard task. However, the more sensitive detection (sub µg.L^{-1}) by ICP/MS using as chromatographic detector has been demonstrated. Consequently, the high resolving capacity of GC and the high sensitivity capability of ICP/MS have made this combination the most efficient and attractive for speciation analysis of silicon in the main fields of interest.

This state of art shows different techniques for silicon speciation. Despite the performances of the classical analytical tools, there remain limitations concerning sensitivity and selectivity in complex matrices. For that reason, the coupling of GC-ICP/MS allowing mass interferences resolution offers promising perspectives and deserves further developments to unravel silicon structures.

Conclusions bibliographiques et Méthodologie

Conclusions bibliographiques

Le premier chapitre a permis de définir l'origine et l'impact du silicium dans les produits pétroliers. Le second chapitre s'est intéressé aux différentes méthodes analytiques disponibles afin de réaliser le dosage total de cet élément mais également sa spéciation nécessaire à la détermination des composés silicés présents dans les charges d'hydrotraitement et potentiellement poisons pour les catalyseurs.

Le silicium (Si) provient de la dégradation thermique des agents antimousse de type PDMS utilisés lors de l'extraction du pétrole brut et des étapes de raffinage. Malgré sa stabilité thermique jusqu'à 300°C sous atmosphère inerte, le PDMS se dégrade et conduit majoritairement à la formation de siloxanes cycliques (D_n) mais également à d'autres composés silicés inconnus. Il est nécessaire de souligner que la présence d'impuretés et les conditions de dégradation (rampe de température, air, N_2, H_2O, hydrocarbures dans les procédés de transformation) vont avoir un impact sur la nature des espèces silicées formées. Si l'étude de la dégradation du PDMS dans des conditions similaires aux procédés de raffinage n'a jamais été effectuée, celle dans l'environnement a montré la formation de composés silicés réactifs et pouvant donc évoluer au cours du temps, notamment par hydrolyse ou condensation. La réactivité des espèces silicées et leur possible évolution s'avèrent donc critiques pour ce travail et nécessitent de s'assurer de la réalisation d'une spéciation dans des échantillons représentatifs. En d'autres termes, les outils analytiques devront être appliqués à des échantillons représentatifs des conditions appliquées dans les procédés pétroliers afin de mettre en évidence les composés silicés réellement formés et donc présents au moment de l'empoisonnement.

La concentration initiale en PDMS injectée est comprise entre 1 et 20 $mg.kg^{-1}$ selon la charge à démousser et explique donc que les concentrations en silicium soient retrouvées à l'état de traces dans les différentes charges d'hydrotraitement. Ces teneurs sont généralement mesurées par ICP-OES et ICP/MS entre quelques centaines de µg de $Si.kg^{-1}$ et quelques mg de $Si.kg^{-1}$ dans les produits pétroliers et nécessitent donc de disposer de techniques analytiques sensibles et sélectives (Figure 2-9). Les faibles concentrations mises en jeu associées à la complexité des matrices en termes de nombre de composés laissent présager de la difficulté de réaliser la spéciation du silicium dans ces produits. De plus, les sources de contamination mises en évidence lors de l'étude bibliographique sont problématiques et devront être minimisées grâce à des solutions adaptées. Ces phénomènes renforcent donc le challenge analytique à relever dans ce travail.

D'après l'état de l'art effectué, des techniques séparatives (GC, LC) couplées à une détection spécifique (SIM (MS), AED, ICP) sont les outils analytiques les plus adaptés pour les études de spéciation du silicium, nécessitant une sélectivité et une sensibilité importantes. Néanmoins, ces couplages nécessitent de disposer des standards analytiques pour obtenir une identification complète de la molécule. C'est pourquoi, l'utilisation de la spectrométrie de masse (MS/MS, FT-ICR/MS) offre également de très bonnes perspectives pour notre étude au niveau de la caractérisation des espèces silicées.

Méthodologie de recherche

Cette partie a pour but de définir la méthodologie de recherche adoptée dans mon travail de thèse en fonction des verrous mis en évidence grâce à l'état de l'art effectué précédemment. La Figure 2-9 présente la démarche adoptée pour parvenir à établir une spéciation du silicium qui soit représentative des molécules présentes au moment de l'empoisonnement.

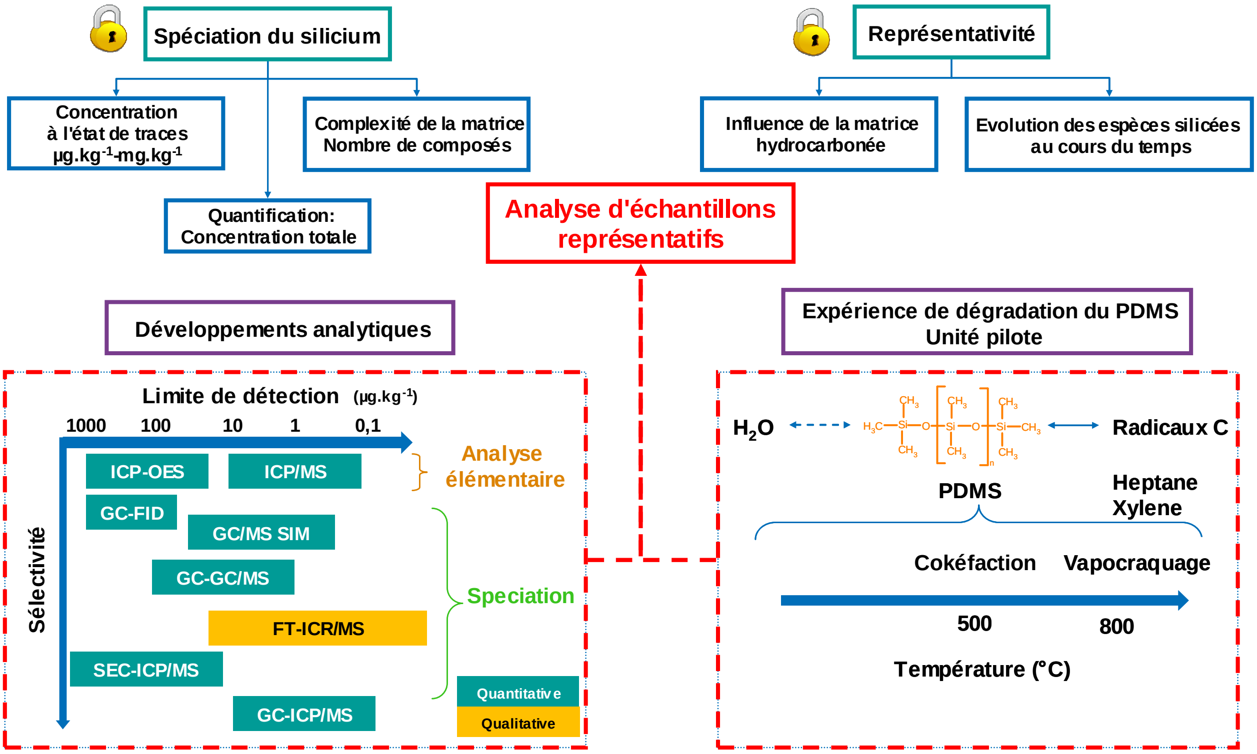


Figure 2-9. Méthodologie de recherche mise en place pour la spéciation du silicium dans les produits pétroliers

Pour parvenir à caractériser les molécules silicées à l'état de traces dans une matrice pétrolière très complexe en termes de nombre de composés présents, il est nécessaire de s'orienter vers des techniques analytiques sensibles et sélectives. Des solutions adaptées pour minimiser les problèmes de contamination devront également être mises en place. Dans cette optique, plusieurs développements analytiques ont été proposés autour de deux principaux outils : la chromatographie en phase gazeuse (GC) couplée à différents détecteurs (FID, MS et ICP/MS) et la spectrométrie de masse à résonnance cyclotronique ionique et à transformée de Fourier (FT-ICR/MS). Afin d'augmenter la sélectivité, l'ajout d'une dimension de séparation en GC couplée à la spectrométrie de masse sera également investiguée, notamment pour l'identification des composés silicés, uniquement détectés par leur temps de rétention par GC-ICP/MS (Figure 2-9). Les développements analytiques des différentes techniques seront présentés dans la partie B et appliqués à des échantillons d'essences ou de naphta provenant de divers procédés de raffinage. En effet, il s'agit des coupes essences pour lesquelles le silicium pose d'importants problèmes d'empoisonnement notamment au niveau des procédés d'hydrogénation.

Le problème de représentativité souligné par la possible formation de composés de dégradation réactifs s'avère crucial dans ce travail et sera abordée dans la partie C. En effet, les composés silicés formés peuvent évoluer soit par des réactions radicalaires, soit par des réactions de condensation ou d'hydrolyse. Les échantillons actuellement prélevés en raffinerie sont analysés après plusieurs mois et ne sont donc pas représentatifs des espèces initialement formées. Pour lever ce verrou, une expérimentation de dégradation à haute température a été menée. La réalisation de ce travail est complexe à mettre en place en raison des températures nécessaires (500-800°C), de la disponibilité des unités, des coûts engendrés et des démarches techniques à effectuer. Cette étude a donc démarré par la recherche et le choix d'une unité pilote au sein d'IFPEN. Après avoir défini les conditions opératoires des tests, un travail important de modification de l'unité pilote associé à la définition de la maquette analytique ont été entrepris. Le but de ce travail est d'une part d'étudier l'influence des hydrocarbures dans des conditions de craquage thermique sur la dégradation du PDMS, et d'autre part de réaliser une spéciation sur des échantillons frais (suppression du délai entre prélèvement et analyse) afin de limiter l'évolution possible des espèces silicées au cours du temps (Figure 2-9).

Cette approche, composée de développements d'outils analytiques innovants et d'une expérimentation pilote, doit permettre l'analyse d'échantillons représentatifs afin de déterminer les structures chimiques des composés silicés réellement présents dans les charges d'hydrotraitement au moment de l'empoisonnement (Figure 2-9).

Partie B. Développements analytiques

Introduction

Comme nous l'avons mentionné précédemment, aucune méthode analytique pour la spéciation du silicium dans des produits pétroliers n'a été reportée dans la littérature en amont de ma thèse. D'après l'étude bibliographique, des développements analytiques, basés sur des techniques sélectives et sensibles, doivent être mis en place. Cette partie est divisée en trois chapitres et a pour but de présenter ces différents développements effectués au cours de mon travail de thèse afin de déterminer la structure des composés silicés et leur quantité relative.

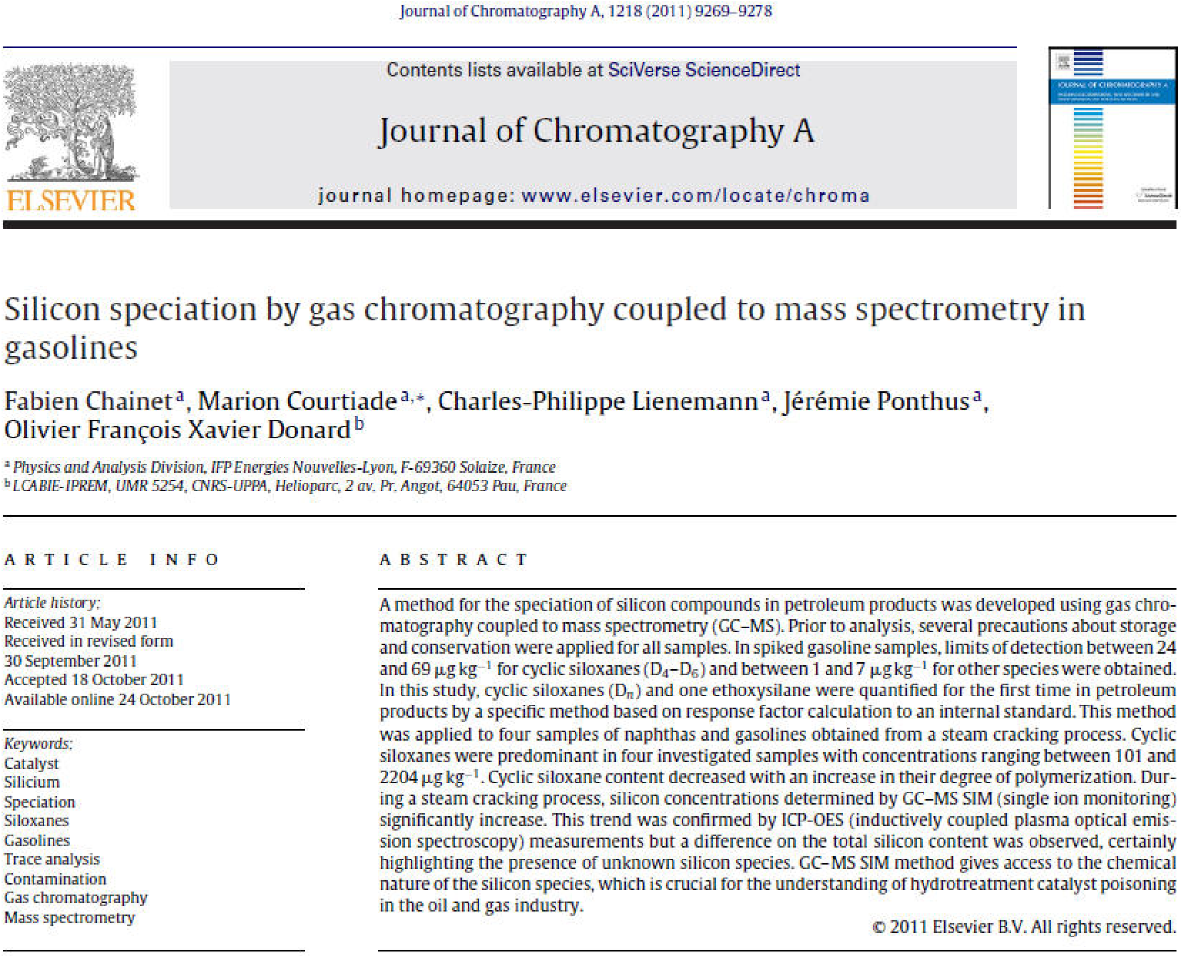
D'après l'état de l'art effectué précédemment, la GC/MS SIM s'avère être un outil adapté pour la détection et la quantification des composés silicés connus. Grâce aux travaux antérieurs de la littérature sur la dégradation du PDMS et sur les tests d'empoisonnement du silicium, une première spéciation d'une dizaine de composés silicés connus avec la technique GC/MS SIM a été effectuée dans des échantillons de naphtas et d'essences issus d'un procédé de vapocraquage (Chapitre 3). Ce travail a fait l'objet d'une publication dans **Journal of Chromatography A** (J. Chromatogr. A) en 2011.

Au sein du Chapitre 4, la suite de mon travail avec le développement d'une méthode par ESI-FT-ICR/MS associée à la construction de diagrammes de Kendrick en utilisant un logiciel développé au sein d'IFPEN présente pour étudier les composés silicés contenant un groupement protonable. Outre l'approche inédite par ESI-FT-ICR/MS utilisée dans ma thèse, l'application d'une fonction spécifique du logiciel sur des composés silicés connus du mélange test a permis de rechercher des composés silicés inconnus, qui diffèrent soit par leur nombre d'alkylation (CH_2), soit par leur nombre d'insaturations (double bond equivalent, DBE) par rapport aux composés modèles. Cependant, la structure développée des composés ne peut être obtenue en ne tenant compte que de ces deux informations. Ce Chapitre s'appuie sur un article de recherche publié dans le journal **Analytical Chemistry** (Anal. Chem.) en 2012.

La détermination de la structure chimique des composés silicés est un des principaux objectifs de mon travail. Dans cette optique, j'ai développé une approche analytique entre la GC-ICP/MS (section 5.1) et la GC-GC/TOFMS (section 5.2) qui est décrite dans le Chapitre 5. La GC couplée à la détection spécifique de l'ICP/MS a été utilisée pour détecter les composés silicés présents (section 5.1). Néanmoins, l'identification des molécules par cette seule technique nécessite de disposer du standard analytique. Cette section a été rédigée sous la forme d'un article en vue d'une future publication dans **Journal of Analytical Atomic Spectroscopy** (J. Anal. At. Spectrom.). Des travaux complémentaires hors du cadre de ma thèse doivent être effectués au cours du mois de Septembre 2012 pour finaliser cette approche.

Afin de pouvoir obtenir une identification structurale de ces composés sur la base des temps de rétention obtenus par GC-ICP/MS, un couplage entre la chromatographie en phase gazeuse "heart-cutting" (GC-GC) et un spectromètre de masse à temps de vol (TOFMS) a été développé pour l'analyse de composés cibles dans une matrice complexe (section 5.2). Cette section fait actuellement l'objet d'une publication en cours d'acceptation dans **Journal of Chromatography A** (J. Chromatogr. A). Dans notre cas précis, à partir des temps de rétention des composés silicés déterminés par GC-ICP/MS mais également par GC/MS, l'utilisation de la même première colonne en GC-GC/TOFMS a été testée pour tenter de retrouver les composés silicés par leur temps de rétention. Néanmoins, en raison de la complexité des matrices pétrolières, les composés silicés d'intérêt sont coélués avec la matrice. En effet, contrairement à l'ICP/MS, la détection TOFMS n'est pas sélective des composés silicés. C'est pourquoi au temps de rétention déterminé par GC-ICP/MS, la fraction contenant le composé silicé pourra être envoyée vers la seconde colonne de sélectivité différente pour être séparée afin d'obtenir le spectre de masse et par la suite une information sur la structure chimique de l'espèce silicée. Dans cette section 5.2, nous présentons donc le développement du couplage GC-GC/TOFMS et sa validation pour la détection et la quantification de plusieurs molécules silicées dans un naptha issu d'un procédé de cokéfaction. Son application pour la caractérisation des molécules présentes dans la fraction liquide des effluents de dégradation sera présentée par la suite.

Chapitre 3. Silicon speciation by Gas Chromatography coupled to Mass Spectrometry in gasolines



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Silicon speciation by gas chromatography coupled to mass spectrometry in gasolines

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ABSTRACT

A method for the speciation of silicon compounds in petroleum products was developed using gas chromatography coupled to mass spectrometry (GC–MS). Prior to analysis, several precautions about storage and conservation were applied for all samples. In spiked gasoline samples, limits of detection between 24 and 69 $\mu g\,kg^{-1}$ for cyclic siloxanes (D_4–D_6) and between 1 and 7 $\mu g\,kg^{-1}$ for other species were obtained. In this study, cyclic siloxanes (D_n) and one ethoxysilane were quantified for the first time in petroleum products by a specific method based on response factor calculation to an internal standard. This method was applied to four samples of naphthas and gasolines obtained from a steam cracking process. Cyclic siloxanes were predominant in four investigated samples with concentrations ranging between 101 and 2204 $\mu g\,kg^{-1}$. Cyclic siloxane content decreased with an increase in their degree of polymerization. During a steam cracking process, silicon concentrations determined by GC–MS SIM (single ion monitoring) significantly increase. This trend was confirmed by ICP-OES (inductively coupled plasma optical emission spectroscopy) measurements but a difference on the total silicon content was observed, certainly highlighting the presence of unknown silicon species. GC–MS SIM method gives access to the chemical nature of the silicon species, which is crucial for the understanding of hydrotreatment catalyst poisoning in the oil and gas industry.

3.1 Introduction

Silicon and its chemical species are of considerable importance in the oil and gas industry. More specifically, by affecting the performance of hydrotreatment catalysts [43], silicon can induce catalytic deactivation and important economic losses due to untimely catalyst replacement [2]. Thus, silicon species must be identified and quantified to improve petroleum refining processes.

In petroleum products, silicon compounds could appear in many organic forms (siloxanes, silanes, silanols) at very low concentration levels [14]. This presence is mainly due to antifoaming agents added in feeds to avoid emulsions in refinery processes such as cocker or visbreaking, steam cracking, distillation but also as an additive to improve oil recovery from the reservoir [5, 30, 50]. Polydimethylsiloxane (PDMS), consisting of a structural unit of –

$(CH_3)_2SiO$-, is the most important silicone used for consumer goods [73] and for industrial applications such as antifoaming [30]. In spite of its properties of low surface tension and initial great thermal stability [7], it degrades itself around 300°C and induces many silicon compounds which are not well-known yet. PDMS degradation at high temperature (500-800°C) under N_2 or O_2 was studied and cyclic siloxanes (D_3-D_{13}) are the main degradation products with the presence of linear siloxanes, silanols and silanes [8-11]. On the contrary, due to the instability of several silicones [86, 90], the reactivity at high temperatures in petroleum products and the chemical nature of silicon species are unknown. By acting as a poison, silicon causes severe catalytic deactivation by adsorption on catalyst surface [43, 45]. Several studies were achieved with standard molecules (ethoxysilanes, silanes) in order to simulate the poisoning effect of silicon compounds and understand mechanisms. However, the state of art in silicon poisoning reported different effects of silicon adsorption depending on catalyst [32], molecule [49] and experimental conditions [45]. Consequently, the understanding is very difficult without information about silicon speciation.

The speciation of Si appears as a key challenge for improved refining process. Up to now, this issue had been well identified but only addressed through the total determination of silicon in the different products. These results have displayed total concentration levels ranging from µg.kg^{-1} of Si up to some mg.kg^{-1} of Si measured by elementary analysis. Determination of total silicon was achieved by ICP-OES [166] (inductively coupled plasma optical emission spectroscopy) with detection limits around 4 µg.kg^{-1} of Si in xylene matrices [166] or by ICP/MS (inductively coupled plasma mass spectrometry) with detection limit of 0.88 µg.kg^{-1} of Si in petroleum products [254] but no information about the molecular identification was provided. Nevertheless, octamethylcyclotetrasiloxane (D_4) has been identified at high concentration by NMR (nuclear magnetic resonance) in contaminated gasolines by unleaded fuels with concentration ranging between 30 to 110 mg.kg^{-1} of Si but this method is not able to achieve speciation at trace levels in complex matrices [70]. More recently, HPLC (high pressure liquid chromatography) combined to ICP/MS was applied to the speciation of standard silicon compounds in xylene [254]. Pure products commercially available were not totally eluted with NP (normal phase)-HPLC and the method can not be applied to silicon speciation in petroleum products with these chromatographic conditions without any further developments. For this reason, methods for silicon speciation in petroleum products are necessary and will be consistent with the total silicon content obtained by elementary analysis.

Two recent reviews have been published in 2006 dealing with silicone analysis and its artifacts and in 2011 focusing on silicon speciation by hyphenated techniques, respectively by Varaprath *et al.* [85] and Chainet *et al.* [14]. According to these latter studies, contamination problems and artifacts associated to very low concentrations generate a real analytical challenge [14, 85]. Specific parts concerning GC instrument and sample storage must be used to minimize these phenomena. Indeed, the matrix complexity relative to compound number associated to contamination, instability and trace level presence makes silicon analysis very hard to achieve. According to Varaprath *et al.* [85], GC/MS is one of the most sensitive technique when it is performed in SIM mode (single ion monitoring). This technique is the most employed in silicon speciation but never in petroleum products [14]. Moreover, it allowed selectivity to other molecules present in the matrix, particularly necessary in organic matrices such as light petroleum products eluted by GC. More recently, determination of cyclic and linear siloxanes has been successfully performed by GC/MS SIM in biogas [255, 256], indoor dust [257], soils [258], water [201, 259] and sediments [259, 260]. Chromatographic separation was generally achieved on a column constituted of 5% phenyl-95% PDMS groups. Limits of detection between 0.2 µg.kg^{-1} and 11 µg.kg^{-1} were obtained after a liquid-liquid extraction for D_4-D_6 in indoor dust and sediments [257, 260].

The aim of this study is to develop a sensitive and selective method for silicon speciation in light petroleum products, such as naphthas and gasolines and to improve the understanding of catalyst poisoning. Prior to the analysis, precautions concerning the minimization of pollution by cyclic siloxanes and sample storage were applied. Moreover, a procedural blank was carried out to take into account potential contamination. In this work, several silicon species (Table 3-1), based on PDMS degradation products and previous poisoning tests with model molecules, were chosen and analyzed by GC/MS SIM. Sensitivity and selectivity were also evaluated in acetone and especially in spiked gasoline by GC/MS SIM because of the complexity of petroleum products as demonstrated by GC-FID (flame ionization detector). Validation concerning repeatability, linearity and detection limits was achieved in order to apply our method to real products. Samples coming from a steam cracking process were analyzed by GC/MS SIM and quantified by a specific method based on the calculation of response factors. Moreover, ICP-OES measurements were achieved to determine total silicon levels. These results were compared with our GC/MS SIM method to evaluate the consistency between elementary analysis and speciation analysis concerning the total silicon content.

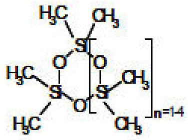
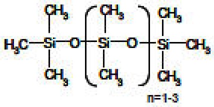
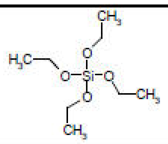
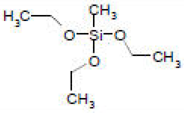
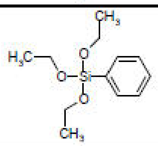
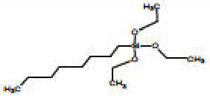
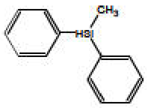
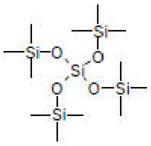
3.2 Materials and Methods

Prior to the analysis of standards and samples, contamination coming from the presence of cyclic siloxanes (D_n) in different parts of the gas chromatograph such as inlet or column bleeding were investigated [14]. It must be emphasized that pollution problems in trace analysis is of considerable importance and contributes to limit sensitivity and affect quantitative analysis. Consequently, several experiments to minimize contamination were carried out and will be further discussed in the Results and Discussion part.

3.2.1 Standards and Solutions

The selection of 12 commercially available silicon compounds is based on the actual knowledge of silicon chemistry in the petroleum industry. Individual standards of D_n (D_3-D_6), L_n (L_3-L_5) and tetrakis(trimethylsilyloxy)silane (M_4Q), used as an internal standard were purchased from Sigma-Aldrich (Lyon, France). Diphenylmethylsilane (J) and ethoxysilanes (B, C, D and H) were provided by Interchim (Montluçon, France). Acetone of LV-GC grade, especially for trace analysis, was obtained from Biosolve Chemicals (Valkenswaard, Netherlands). A mixture of standard molecules, belonging to different families represented by colours (Table 3-1), was prepared with a concentration of 1 mg.kg^{-1} in acetone and different dilutions were achieved to evaluate limits of detection (LOD_s) and linearity. Solutions and standards were stored in 30 ml high density polyethylene bottles at 4°C. Before analysis, samples were transferred in polypropylene vials with PTFE only septa, provided by VWR (Fontenay sous Bois, France) in replacement of classical septa made of silicones.

Table 3-1. Silicon compound properties

Molecules	Abbreviations	B.P. (°C)	M.M (g.mol^{-1})	Si %	Structure
Cyclic Siloxanes					
Hexamethylcyclotrisiloxane	D_3	134	222	37.76	
Octamethylcyclotetrasiloxane	D_4	175	296		
Decamethylcyclopentasiloxane	D_5	211	370		
Dodecamethylcyclohexasiloxane	D_6	245	444		
Linear Siloxanes					
Octamethyltrisiloxane	L_3	153	236	35.51	
Decamethyltetrasiloxane	L_4	194	310	36.05	
Dodecamethylpentasiloxane	L_5	210	384	36.38	
Ethoxysilanes					
Tetraethoxysilane	D	168	208	13.44	
Triethoxymethylsilane	H	143	178	15.73	
Phenyltriethoxysilane	B	265	240	11.68	
Triethoxyoctylsilane	C	168	276	10.16	
Silane					
Diphenylmethylsilane	J	266	198	14.12	
Internal standard					
Tetrakis(trimethylsilyloxy)silane	M_4Q	106	384	36.46	

3.2.2 Samples

All petroleum samples (Table 3-2) were supplied by AXENS (Rueil Malmaison, France) and taken from a steam cracking process at different run times and days. Steam cracking is an important process for the petrochemical industry consisting of the production of light alkenes (ethylene, propylene, butadiene) and aromatics (benzene, toluene and xylene) from ethane, LPG (light petroleum gas), gasoline, and/or heavy cuts of crude oil, without catalysts at

800°C and in presence of steam. The products obtained with this process are directed to further processes where catalysts can be poisoned if silicon is present. Two naphtha samples (N_1 and N_2), representing process entry (feeds), and two pyrolysis gasolines (G_3 and G_5), representing steam cracking process exit (end products) without any further processing on downstream catalytic process, were analyzed by the GC/MS method. Moreover, these samples were also analyzed by ICP-OES to determine total silicon. Gasoline A (Table 3-2), with no traces of silicon (previously measured by ICP/MS) was also used to spike known silicon compounds for matrix effect study and limit of detection evaluation in real samples. All samples were spiked with 100 µg.kg^{-1} of M_4Q (internal standard) in order to control mass spectrometer variations and to achieve silicon quantification.

Table 3-2. Composition summary for real samples

Samples	Abbreviations	Methods		
		ASTM D2887	NF EN ISO 12185	According to
		Boiling range (°C)	Density (g.cm^{-3})	Total silicon (mg.kg^{-1})
Gasoline A	G_A	10→197	0.7306	not detected by ICP/MS (LOD of 5 µg.kg^{-1} of Si)
Naphtha 1	N_1	37→177	0.7006	528
Naphtha 2	N_2	38→181	0.7015	556
Gasoline 3	G_3	23→226	0.8063	1016
Gasoline 5	G_5	23→250	0.8587	2527

3.2.3 Apparatus

ICP-OES

ICP-OES analysis was carried out with an Iris Advantage 200 (Thermo Jarrel Ash, Franklin, Massachusetts, USA) operating at 27.12 MHz in which signals were axially taken. The system was equipped with a glass pneumatic concentric nebulizer (TR-30-A1, Meinhard Glass Products, Golden, Colorado, USA) fitted to a 12 cm^3 glass single pass spray chamber (torch integrated sample introduction system, TISIS). The TISIS was equipped with a heating tape wound around it and a thermocouple (JP Selecta, Barcelona, Spain) to carry out experiments at high temperatures (h-TISIS) [165]. These systems allowed the minimization of the impact of silicon chemical form, that was demonstrated significantly dependent on the ICP-OES response [166]. Prior to measurements, each sample was diluted by 1:4 in xylene.

GC-FID

Detailed analysis of hydrocarbons was performed using an Agilent 6890 gas chromatograph (Agilent Technologies, Massy, France) following ASTM D6733 [261]. The injection was achieved at 250°C with a 1:200 split ratio and an injection volume of 0.5 µl. Separation was achieved by a 50 m PONA column (0.20 mm i.d., 0.50 µm film thickness) from J&W Scientific (Folsom, California, United States). The oven temperature varies from 35°C to 114°C at 1.1°C.min^{-1} and then from 114 to 280°C at 1.7°C.min^{-1}. Helium (99.99% Air liquide, France) was used as a carrier gas with a constant pressure of 105 kPa. Analytes are detected with a FID at 320°C.

GC/MS

Samples were analyzed using a gas chromatograph-mass spectrometer Thermo Scientific GC TRACE DSQ (Thermo Fischer scientific, Courtaboeuf, France). Separation was achieved by a low bleed capillary column DB-5 MS UI (30mx0.25 mm i.d., 0.25 µm film thickness) from J&W Scientific (Folsom, California, United States). A volume of 0.1 µl of real samples was injected using a split/splitless injector with a splitless time of 0.2 min through a Merlin microseal valve (silicone-free) (Thermo Fisher scientific, Courtaboeuf, France (silicone-free). Injection temperature of 200°C was used with helium as a carrier gas at 0.9 ml.min^{-1} constant flow rate. The column oven temperature was programmed from 30°C (7 min) to 50°C at 2°C.min^{-1}, then to 60°C at 1°C.min^{-1}, then increased to 120°C at 2°C.min^{-1} and followed by a final temperature ramp of 20°C.min^{-1} to 300°C and held for 2 min. The total time for a run was 68 min. However, a second temperature program from 30°C to 120°C at 5°C.min^{-1} and then increased at 20°C.min^{-1} to 300°C (2 min) was also performed for standard mixture in acetone. The total run was reduced to 31 min.

The mass spectrometer equipped with electron impact ionization source at 70 eV and 200°C was operated in full scan mode (m/z 20 to 500) and single ion monitoring mode (SIM). For SIM experiments, target ions of each compound were selected, from their mass spectra previously obtained in full scan mode, with a dwell time of 100 ms and mass accuracy of *m/z* ±0.5. The mass spectra were compared against the NIST database (National Institute of Standards and Technology, Gaithersburg, MD, USA version 2005).

The SIM program consisted in one acquisition window starting at 7.00 min in which 3 ions listed in Table 3-3 were monitored to conserve a correct identification. For quantification, only one ion (bold) was used and a specific method based on the calculation of response factors compared to an internal standard was applied. The SIM program was defined in different segments depending on the retention times of silicon species obtained by GC. For triethoxymethylsilane (H) and octamethyltrisiloxane (L_3), *m/z* 119, 133, 163 and *m/z* 221, 222, 223, were monitored for identification purposes (Figure 3-2 and Table 3-3). The acquisition in SIM mode was essential in complex matrices such as gasolines to obtain a sufficient sensitivity and selectivity. However, other unknown species, such as unidentified silicon molecules yet or hydrocarbons, would not be detected.

Table 3-3. SIM program used to analyse real samples

Segments	Initial time	Compounds	m/z ions
1	7.00	D_3	**207** 208 209
2	12.00	H L_3	119 133 **163** **221** 222 223
3	18.00	D D_4	149 163 **193** 265 281 282
4	28.00	L_4	73 **207** 295
5	34.00	D_5	73 267 **355**
6	40.50	L_5 M_4Q	**281** 282 369
7	48.00	D_6	73 **341** 429
8	53.00	B	147 162 **195**
9	57.00	C J	119 **163** 164 105 **120** 183

3.3 Results and Discussion

3.3.1 Contamination by cyclic siloxanes (D_n)

Different sources of contamination during silicone analysis have been reported by a previous review [14]. This study showed that vial and inlet septa, made of silicones, caused serious contamination problems by cyclic siloxanes. Column bleeding could generate a background of siloxanes but concentrations are minor compared to the septum bleeding [206]. Moreover, the widespread use of silicones in personal care and consumer products seriously increased these phenomena. Thus, extreme care must be taken in order to minimize sources of siloxane contamination for speciation and analysis, in particular at trace levels.

In this study, specific parts were used in order to minimize contamination problems. Several septa and inlet temperatures were tested and it was observed that the background of siloxanes (D_3-D_8) decreased when lower inlet temperature was applied. To suppress the inlet septum influence, it was replaced by a Merlin microseal valve (silicone-free) and an inlet temperature of 200°C was applied. A low-bleed capillary column, DB-5 MS UI, was also used to reduce siloxane background release.

Concerning sample storage, vials made in polypropylene were chosen to avoid a possible adsorption of silicones on glassware [86]. First experiments were achieved with silicone/PTFE septa vials and have showed a release of siloxanes (D_3-D_8) in samples after several injections through the same septum. Thus, PTFE only septa were used for all analysis. Despite these precautions, an internal contamination located in the GC injector released $D_{4\text{-}6}$ in all samples. Different tests on splitless time (0.2-20 min) have demonstrated that siloxane levels increased with splitless time. The pollution may be generated by purge septum or split inlet valve. To minimize this pollution, a splitless time of 0.2 min and a procedural blank were applied.

Before each analysis, an acetone blank and gasoline A spiked with M_4Q at 100 µg kg^{-1} were directly analyzed (without any concentration or preparation steps) in order to determine cyclic siloxane backgrounds (D_4-D_6). Using our quantification method based on the calculation of response factor, D_4-D_6 levels in gasoline A were measured. This contamination appeared to be repeatable day to day and concentrations of D_4, D_5 and D_6 are respectively 57, 24 and 29 µg.kg^{-1} for 10 replicates taken from different weeks. Sanchez *et al.* [258] and Flassbeck *et al.* [117] have respectively reported trace quantities of D_n in THF and ethyl acetate in blanks using GC/MS in SIM mode. For example trace quantities of D_4 (11-16 µg.l^{-1}) and D_5 (25-31 µg.l^{-1}) were detected during procedural blank when ethyl acetate was used, while no contamination was detected with hexane [258]. The presence of cyclic siloxanes in blanks was reported by other workers [82, 83, 262] and it was necessary to perform a procedural blank during the analysis of siloxanes. Therefore, concentrations of D_n recovered in blank of gasoline A were subtracted from real sample values. The background of $D_{4\text{-}6}$ is high but in the same order for D_5 compared to Sanchez *et al.* [258] when using ethyl acetate, and makes trace level quantification a hard task for these three compounds.

3.3.2 Chromatographic determination

GC-FID was firstly used to demonstrate the complexity of gasoline samples but sensitivity and selectivity for silicon speciation at trace levels were not possible. After taking into account the different source of contamination and performing method optimization, GC/MS SIM was applied to silicon species at trace levels in acetone, spiked gasoline for validation and especially to petroleum products to improve the chemical nature of silicon molecules.

3.3.2.1 Analysis of hydrocarbons

Gasoline is a complex organic matrix with generally more than 200 molecules. Figure 3-1 illustrates a GC-FID chromatogram obtained for gasoline A analysis. Paraffins (52.0%), naphthens (15.7%), aromatics (11.1%) and olefins (21.2%), from 4 to 15 carbon atoms were identified. The number of hydrocarbons associated to trace levels of silicon in petroleum products makes speciation a very hard task. Previous work by GC-FID on silicon compounds have shown detection limits ranging from 100 to 700 µg.kg^{-1} and were not adapted to total silicon concentrations measured in feeds (Table 3-2). Moreover, according to boiling ranges of silicon compounds (Table 3-1) and gasoline cut (Table 3-2), a concentration step is relatively hard to achieve that also preserves sample integrity. Consequently, GC/MS was applied in SIM mode in order to obtain sufficient sensitivity and selectivity for silicon speciation in gasolines.

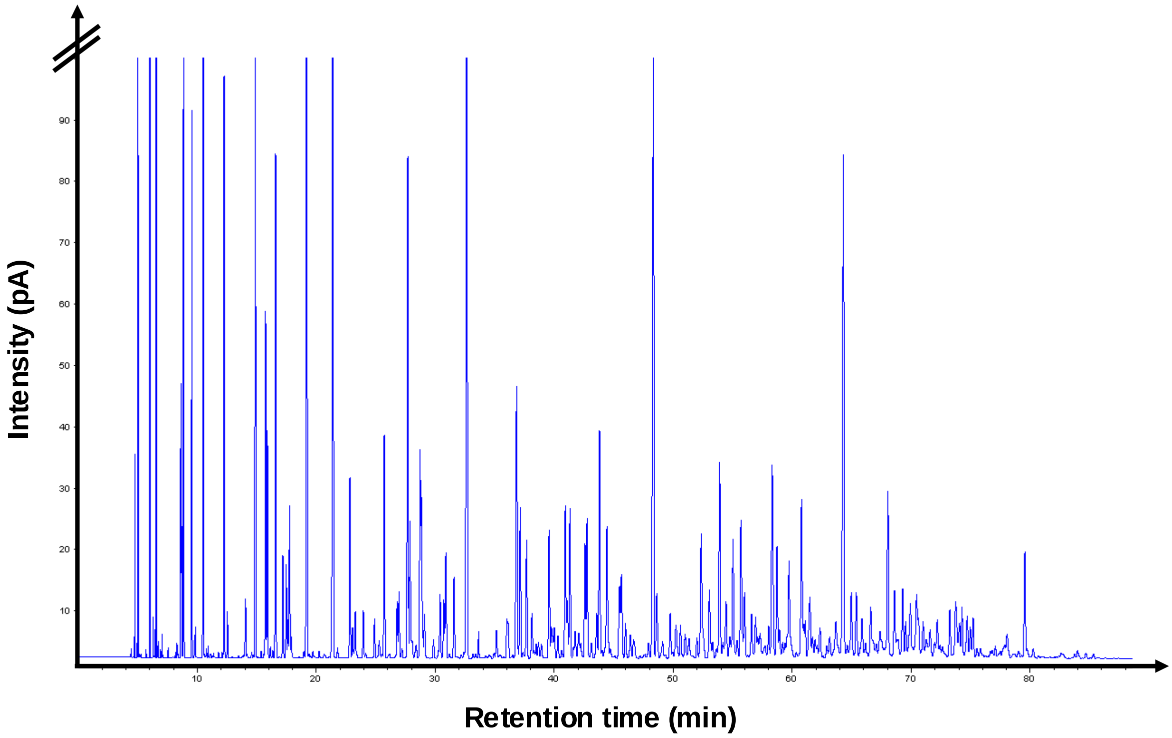


Figure 3-1. GC-FID chromatogram of gasoline A

3.3.2.2 Speciation of silicon compounds

The chromatographic method was firstly applied in acetone with a 0.5 µl injection volume and a temperature program of 5°C.min^{-1}. However, co-elution between D (168°C) and D_4 (175°C) occurred and a poor separation of silicon compounds in gasoline was obtained under these conditions. Thus, to reduce matrix effect, injection volume was reduced to 0.1 µl, splitless time and the temperature program were optimized. The separation by GC/MS SIM of 12 compounds at 50 µg.kg^{-1} belonging to different organosilicon families (Table 3-1) is illustrated in Figure 3-2. Several hydrocarbon molecules eluted at the end of the analysis with the same fragmentation ions than C and J compounds (Table 3-1). Thus, a zoom of the chromatographic area between 61.00 and 62.00 was presented in order to show the correct separation between C and J molecules.

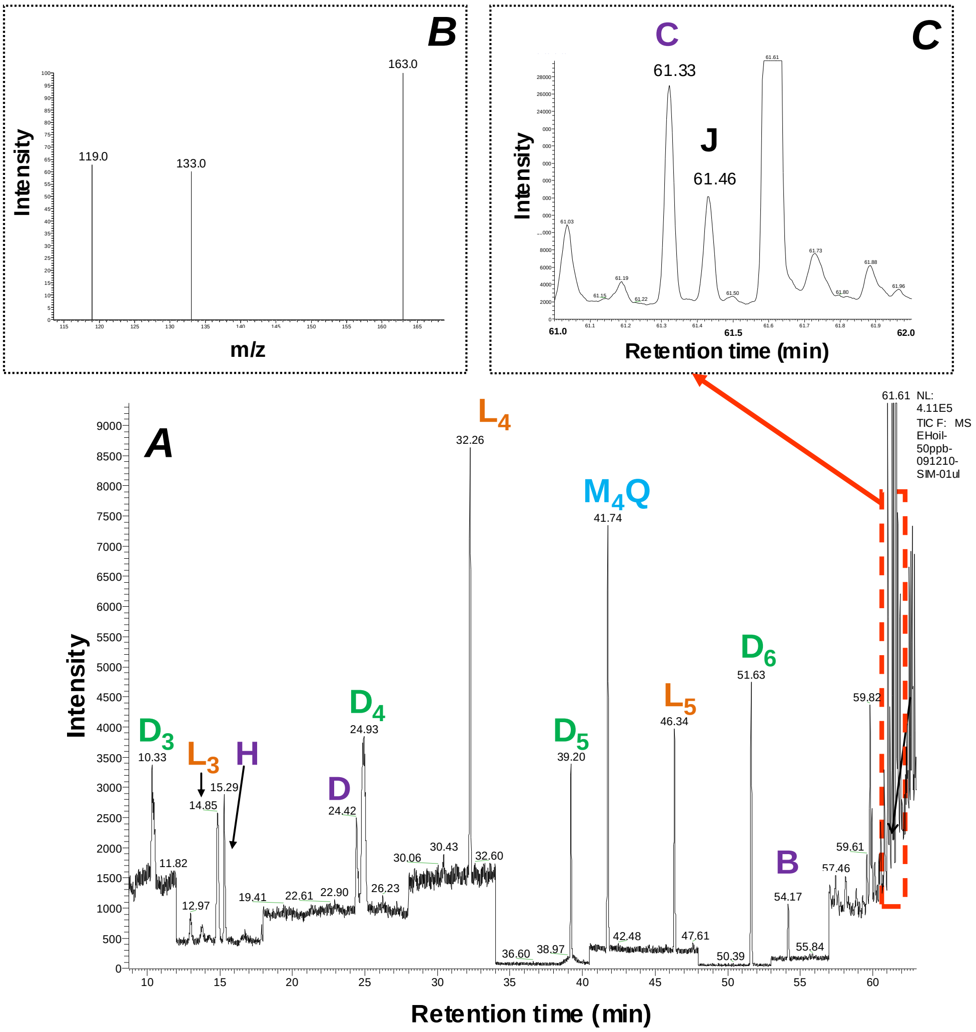


Figure 3-2. (A) GC/MS SIM chromatogram of Gasoline A spiked with 50 µg.kg^{-1} of silicon compounds and 100 µg.kg^{-1} of M_4Q (B) Mass spectrum in SIM mode of H molecule with the 3 ions. (C) GC/MS SIM chromatogram of C and J silicon molecules between 61.00 and 62.00 minutes

3.3.3 Method validation

The total silicon content is of considerable importance in the oil and gas industry. Thus, to make a comparison with elementary analysis, a quantification method allowing sensitivity with limit of detection around 5 µg.kg^{-1} and selectivity was developed and validated in spiked gasoline.

3.3.3.1 Repeatability and linearity

The repeatability of the method was calculated by analyzing five times gasoline A spiked with 20 µg.kg^{-1} of silicon molecules within the same day. Relative standard deviation (RSD) defined as the ratio of standard deviation on the average is calculated on retention times and peak area determination. The RSD obtained for retention times were equal or lower than 0.14% and are ranged between 0.7 and 6.2% for peak area in gasoline. For comparison, RSD values on retention time are lower than 0.1% and peak area are ranged between 0.5 and 6% in acetone. Most of hydrocarbon compounds of gasoline, not detected in SIM mode, eluted until 30 min and contributed to slightly increase RSD on retention times for D_3 to L_4 silicon molecules (Figure 3-2).

Table 3-4. Validation data, limits of detection and quantification of silicon compounds

Compounds	t_R (min)	Linearity		Repeatability [a]		LOD	LOQ
		Equation y=ax+b	r^2	t_R	Peak area	(µg.kg^{-1})	
D_3	10.33	y=0.0099x+0.2751	0.998	0.06	6.2	6.9	23.0
L_3	14.55	y=0.0128x+0.1296	0.998	0.10	2.4	4.7	15.7
H	15.29	y=0.0068x+0.2961	0.998	0.13	4.5	2.0	6.6
D	24.42	y=0.0056x+0.2188	0.998	0.08	5.8	6.5	21.5
D_4	24.93	y=0.0207x+0.0545	0.998	0.14	4.6	57	190
L_4	32.25	y=0.0174x+0.2096	0.999	0.05	2.6	2.6	8.7
D_5	39.20	y=0.0059x+0.1259	0.999	0.03	2.5	24	80
M_4Q	41.74	y=317.66x+4152	0.995	0.01	--	2.0	6.8
L_5	45.34	y=0.007x-0.0091	0.998	0.01	2.5	1.3	4.2
D_6	51.63	y=0.0041x+0.1406	0.998	0.01	2.8	29	97
B	54.17	y=0.0019x+0.0417	0.999	0.02	0.7	4.7	15.7
C	61.33	y=0.0119x+0.2509	0.998	0.04	2.7	1.6	5.4
J	61.46	y=0.0064x+0.332	0.998	0.05	1.2	3.7	12.3

[a] Standard deviation of retention time and peak area (n=5)

The linearity was studied for a concentration range from 100 to 2000 µg.kg^{-1} (100, 200, 500, 1000 and 2000) of silicon molecules in acetone and in gasoline A with 5 points. All investigated solutions were spiked with 100 µg.kg^{-1} of internal standard in order to obtain a relative response compared to M_4Q. This procedure consisted of taking into account MS response variations day by day and to calculate response factors for all compounds. Only the results in gasoline A are presented because contrary to acetone it takes into account the matrix effect. The linearity was also studied between 10 and 100 µg.kg^{-1} but no great variations on relative slope compared to concentration range between 100 to 2000 µg.kg^{-1} have been observed. Results of calibration data for concentration range between 100 to 2000 µg.kg^{-1} are listed in Table 3-4 and showed linearity response for all compounds with correlation coefficients equal or lower than 0.998. Absolute response and detection limit of M_4Q were also indicated in this table.

3.3.3.2 Limits of detection and quantification

The LOD_s and LOQ_s (limits of quantification) were calculated considering a signal to noise of 3 and 10 respectively in gasoline A spiked with 20 µg.kg^{-1} of silicon molecules (Table 3-4). For D_{4-6}, LOD_s and LOQ_s were defined as the mean content in the blanks of gasoline A (n=10) plus 3 or 10 times of its deviation standard, respectively (part 3.3.1). For these compounds, LOD_s are respectively 57, 24 and 29 µg.kg^{-1}, which correspond to LOQ_s of 190, 80 and 97 µg.kg^{-1}. No other molecules were found in the procedural blank. Detection limits between 1.3 and 6.9 µg.kg^{-1} were obtained for other compounds, which correspond to LOQs ranging between 4.2 to 23.0 µg.kg^{-1}. These values are consistent with other previous studies by GC/MS SIM for silicon compounds in soils [90, 258], in biological tissues [117], in consumer products [82, 83] and in other matrices where silicon molecules are of considerable importance [14]. The advantage of the present study is the possibility to operate without any preparation or concentration steps and only with internal standard spiking.

3.3.3.3 Quantification method

Due to the difference on the response of silicon compounds by mass spectrometry, the quantification method is based on the calculation of response factors (R.F.) for each silicon compound against the internal standard M_4Q. The linearity of M_4Q was studied between 10 and 2000 µg.kg^{-1} (10, 20, 50, 100, 200, 500, 1000 and 2000). Results have shown a linear response of the standard with the same tune file with correlation coefficient of 0.995. However, to minimize the response variation of compounds due to mass spectrometer calibration, all compound areas were normalized with the internal standard area. Response factors were calculated following Equation 3-1:

$$\text{R.F.} = \underbrace{\frac{a_{\text{gasolineA}_{\text{rM}}}}{a_{\text{gasolineA}_{\text{M}_4\text{Q}}}}}_{k}\ \text{x}\text{A}_{\text{M}_4\text{Qs}}$$

Equation 3-1. Calculation of response factors (RF) for quantification

where $a_{gasolineArM}$ represents the relative slope of each compound to M_4Q obtained in standard gasoline A, $a_{gasolineAM4Q}$ represents the slope of M_4Q obtained in standard gasoline A and A_{M4Qs} represents the peak area of M_4Q measured in each sample. The ratio k between each molecule relative slope in gasoline A ($a_{gasolineArM}$) and M_4Q absolute slope in gasoline A ($a_{gasolineAM4Q}$) was calculated. The response factor was obtained by the product of the k ratio with M_4Q peak area measured in real sample. For this calculation, b was not significant because it was equal or lower than 1% of the maximal relative area. Previously, response factors were calculated in acetone but matrix effect is very important and considerably influences the quantification results. Moreover, the calculation of response factors in different matrices (naphtha and gasoline) has not show significant variations. Thus, this method takes into account the matrix effect with the internal standard spike in each real sample and avoids mass spectrometer variations day after day.

3.3.4 Application to real samples

Results obtained by GC/MS SIM have shown for the first time the identification and the quantification of several silicon species in the refined products that could be potentially responsible for catalyst poisoning in petroleum products. Results comparison on Si concentrations between elementary analysis and GC/MS SIM was achieved to evaluate the consistency concerning the total silicon content. However, the selectivity of SIM mode and the different response signal observed by plasma based method for these species have hampered the quantification step.

Silicon speciation of 12 compounds was achieved for four petroleum products from a steam cracking unit by the GC/MS SIM method previously developed. GC/MS SIM chromatogram of naphtha 1 (feed) and gasoline 5 (end product), spiked with 100 $\mu g.kg^{-1}$ of M_4Q, are respectively presented in Figure 3-3 and Figure 3-4. The analysis demonstrated the presence of cyclic siloxanes (D_3-D_6), tetraethoxysilane (D) and dodecamethylpentasiloxane (L_5) at different concentrations according to samples. L_5 was only detected in gasoline 5 (Table 3-5). Several compounds, probably hydrocarbons or unidentified silicon species with the same ions as target molecules, were also detected in these samples. Identification of silicon molecules was based on retention time comparison with a standard mixture in gasoline A and on the acquisition of 3 ions per molecule when possible. However, quantification based on the acquisition of one ion was applied to increase selectivity to hydrocarbons.

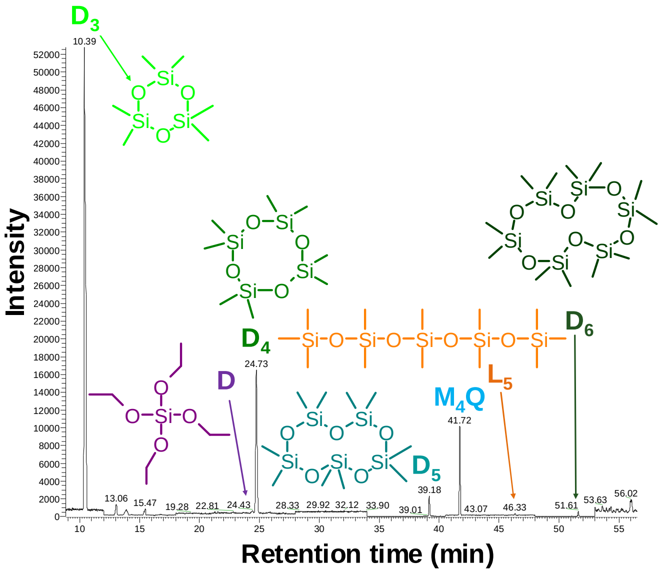


Figure 3-3. GC/MS SIM chromatogram of naphtha 1 spiked with 100 µg.kg^{-1} of M_4Q

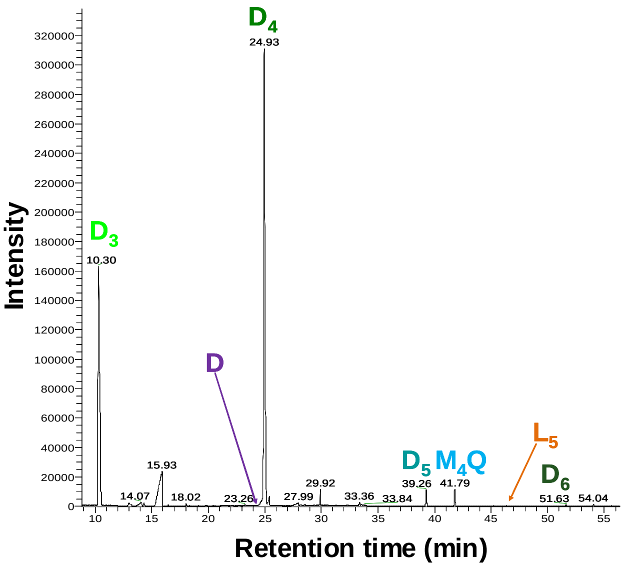


Figure 3-4. GC/MS SIM chromatogram of gasoline 5 spiked with 100 µg.kg^{-1} of M_4Q

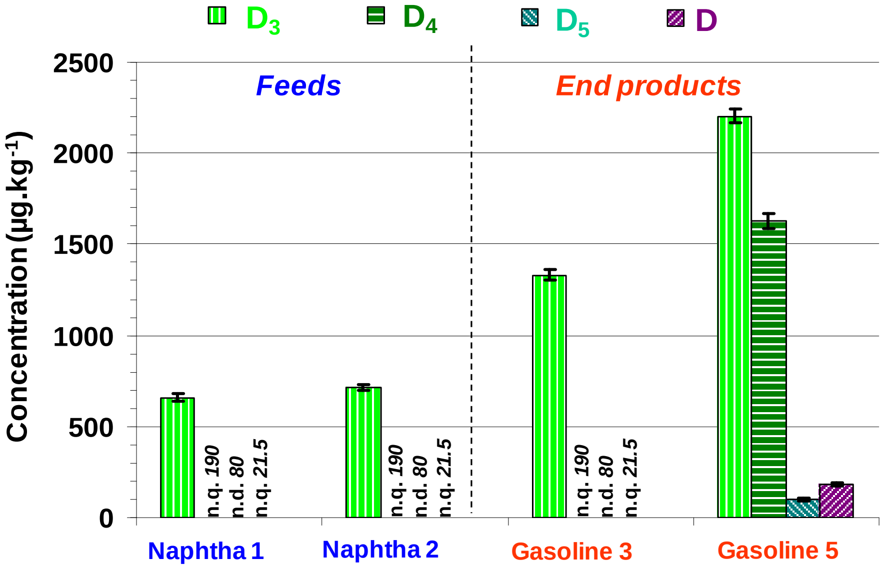
Quantification was performed for 3 replicates (Table 3-5) with the method based on the calculation of response factors. Concentrations, expressed in µg.kg^{-1} or in µg.kg^{-1} of Si for total silicon concentrations by GC/MS SIM are calculated and compared to ICP-OES results. Values are listed in Table 3-5 for all investigated samples in this work. Moreover, organosiloxane distribution in each sample is illustrated in Figure 3-5. The aim of this figure is to show the evolution of silicon molecules through the steam cracking process. D_3 was the major detected compound in all samples with concentrations ranging between 566 and 2204 µg.kg^{-1} (Table 3-5 and Figure 3-5). D_4 was also detected in all products but contamination by cyclic siloxanes (D_4-D_6) allowed the quantification above 190 µg.kg^{-1}. However, D_4 was found at 1627 µg.kg^{-1} in gasoline 5. In 1988, Carduner *et al.* [70] have detected silicon by ICP-OES in unleaded gasoline and have already identified octamethylcyclotetrasiloxane (D_4) by ^{29}Si NMR at -19.55 ppm. However, there is not enough sensitivity by NMR to perform trace speciation analysis [14]. Tetraethoxysilane was detected in four samples but it was only quantified in gasoline 5 at 181 µg.kg^{-1}. Concentrations measured in other samples were above detection limit equal to 6.5 µg.kg^{-1} but could not be quantified. According to Wang *et al.* [40], tetraethoxysilane and other molecules (sulphur or silicon) can be used to avoid coke formation during steam cracking process and could have been intentionally added. After subtraction of background concentrations determined in gasoline A, the method was not able to detect D_5 and D_6 in naphthas and gasoline 3. Except for D_6 and L_5, all other compounds detected in gasoline 5 were quantified, for example, D_5 was recovered at 101 µg.kg^{-1}. The concentrations of cyclic siloxanes tended to decrease with an increase of their degree of polymerization in all investigated products. This trend was also observed in several articles [8, 9, 11] that reported silicon rearrangement products due to thermal PDMS degradation. Experiments were performed with a temperature around 500°C under N_2 flow during the study of polymer stability. The results of three studies showed a similar distribution illustrated in Figure 3-5 for cyclic siloxanes (D_3-D_5) in gasoline 5. In addition Camino *et al.* [11] have detected the presence of dodecamethylpentasiloxane (L_5), cyclic siloxanes (D_n) and various unknown compounds during PDMS degradation at 800°C (similar temperature in steam cracking) under N_2 flow [11]. Cyclic siloxanes with higher polymerization degree ranging between 3 and 13 were also obtained in these previous studies [8, 9, 11]. In this study, cyclic siloxanes with polymerization degree higher than D_6 were not present in light petroleum products due to the fact that their boiling points are greater than the final boiling point of gasoline.

Table 3-5. Concentrations of silicon compounds (µg.kg^{-1} or µg.kg^{-1} of Si) measured in real samples

Samples	Feeds		End products	
Compounds	Naphtha 1	Naphtha 2	Gasoline 3	Gasoline 5
D_3	659±20	714±14	1331±30	2204±35
D_4	n.q. *190*	n.q. *190*	n.q. *190*	1627±39
D_5	n.d. *24*	n.d. *24*	n.d. *24*	101±6
D_6	n.d. *29*	n.d. *29*	n.d. *29*	n.d. *29*
D	n.q. *21.5*	n.q. *21.5*	n.q. *21.5*	181±6
L_5	n.d. *1.3*	n.d. *1.3*	n.d. *1.3*	n.q. *4.2*
Total (µg.kg^{-1})	659±20	714±14	1331±30	4113±97
Total Si (µg.kg^{-1} of Si)	249±8	270±11	503±12	1509±38
(µg.kg^{-1} of Si) by ICP-OES	528±57	556±29	1016±96	2527±128

n.d.: not detected; n.q.: not quantified

The limits of detection (LOD_s) and quantification (LOQ_s) are indicated in italics (Table 3-4)



n.d.: not detected; n.q.: not quantified
The limits of detection (LOD$_s$) and quantification (LOQ$_s$) are indicated in italics (Table 3-5)

Figure 3-5: Concentrations of organosiloxanes (µg.kg^{-1}) in samples before (feeds) and after (end products) steam cracking process

The total concentration in two naphthas (feeds) and two gasolines (end products) are ranging between 659 and 4113 µg.kg^{-1} respectively. Levels recovered in naphtha 1 and naphtha 2 are respectively 659 and 714 µg.kg^{-1} and are nearly the same. On the contrary, a great difference in silicon levels was observed between gasoline 3 with 1331 µg.kg^{-1} and gasoline 5 with 4113 µg.kg^{-1}. Gasoline 5 is the most concentrated sample of organosiloxanes (Table 3-5 and Figure 3-5). No explanations about these differences can be given yet because it greatly depends on feed properties and reactivity. Moreover, no further information about the process was obtained.

According to a comparison between naphtha and gasoline samples, organosiloxane concentrations significantly increase during steam cracking process (Figure 3-5). It was probably due to supplementary silicon molecules added in the process entry to avoid emulsions such as PDMS [30] or to limit coke formation such as silicon-sulphur compounds [40]. In addition, temperature at 800°C and steam make easier the degradation of PDMS and contribute to the formation of silicon compounds in feeds at trace. According to silicon percentage in each molecule (Table 3-1), total silicon concentration in µg kg^{-1} of Si was calculated and compared to ICP-OES measurements which take into account the presence of all silicon species. The increase of silicon concentration during steam cracking and the level ranges between samples were confirmed by ICP-OES results. According to total silicon concentration, the quantification method by GC/MS SIM gives access to nearly 50% of the total content determined by ICP-OES with the current identified molecules for naphthas and gasoline 3 and nearly 60% for gasoline 5 (Table 3-5). These differences can be mainly explained by the selectivity of the SIM detection method, which is not universal for silicon compounds. GC coupled to mass detection performed in SIM mode allows the speciation of 12 selected compounds with quantification limits between 4 and 190 $\mu g.kg^{-1}$. However, SIM mode as defined in the proposed method does not detect unknown compounds. According to Camino *et al.* [10], only PDMS degradation can generate a great number of low molecular weight silicon compounds. Associating to the reactivity during refining processes, reactions between silicon compounds and hydrocarbon radicals probably produce other unidentified silicon compounds included in ICP-OES results. Thus, GC/MS SIM does not take into account all silicon molecules and the difference on the total silicon content measured by ICP-OES can be explained. Concerning ICP-OES results, Sanchez *et al.* [165, 166] have exhaustively studied the dependency of the ICP-OES response with the silicon chemical form. On the 16 silicon compounds investigated in theses previous studies, 5 molecules (D_4, B, C, D and J) are similar to this study and the use of h-TISIS (heated torch integrated sample introduction system) minimized the variation of response factors [165, 166]. However, molecules such as D_3, D_{5-6}, L_{3-5} and H or unknown silicon compounds, potentially present in petroleum samples, were not studied and the different chemical form still slightly modified ICP-OES response factor. For these reasons, comparison on the total silicon content between ICP-OES and GC/MS SIM results is currently a very hard task and need supplementary analytical developments to progress in the identification of new unidentified silicon species.

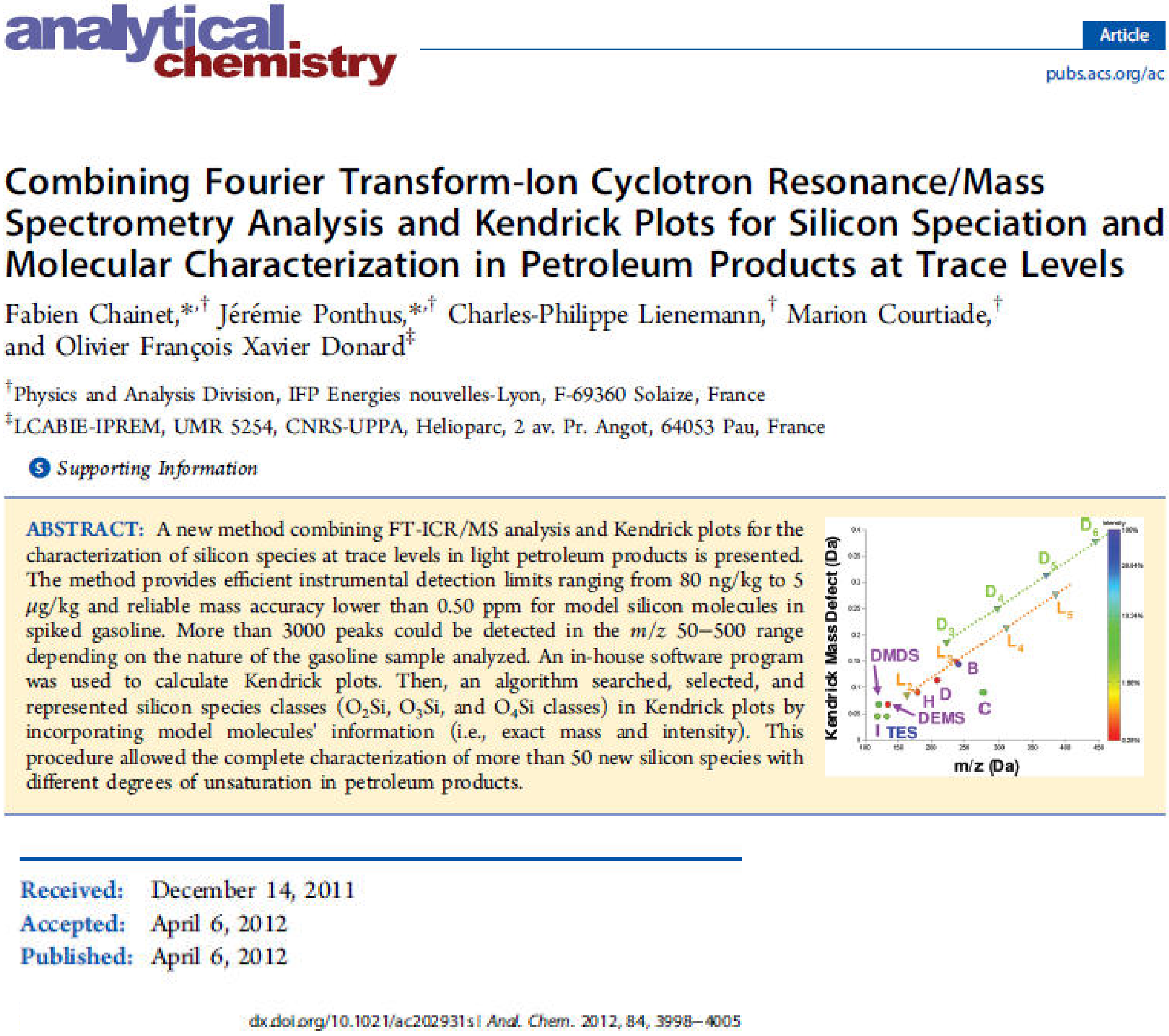
The work presented here gives access to essential information about the nature of silicon compounds in gasolines and contributes to a better knowledge of silicon speciation in petroleum products. Silicon compounds such as cyclic siloxanes (D_3-D_5), linear siloxane (L_5) and ethoxysilane (D) were identified for the first time in real light petroleum products (naphthas and gasolines) but hypothesis relative to links between PDMS added as antifoaming on feeds and silicon compounds in steam cracking process are not evident. The GC/MS method has to be applied to more representative samples in terms of process conditions and waiting time between sampling and analysis. Moreover, GC associated to specific detector should be used to improve results on speciation for the determination of the new unidentified silicon molecules and to be consistent with total silicon measurements by elementary analysis.

3.4 Conclusions

Trace analysis of poisons (Hg, As, Si...) in petroleum products is of great importance considering irreversible poisoning effects induced in hydrotreatment catalysts. For silicon, information about the chemical nature of these species is relatively scarce and development in speciation is essential. The proposed GC/MS SIM method allowed the speciation of 12 silicon compounds at trace levels in gasolines with quantification limits ranged between 4 and 190 µg.kg^{-1}. This study showed the presence of siloxanes and ethoxysilane at very different concentrations. Among these organosiloxanes, cyclic siloxanes (D_n), in particular D_3 and D_4, were found with the highest presence and concentration.

To our own knowledge, this is the first work reporting the speciation of silicon compounds in real petroleum products. These first results providing structural information and quantification about silicon species in gasolines bring a novel knowledge of compounds potentially responsible of catalyst poisoning. These data are essential for catalysis study and highlight the need for further developments in poisoning tests applied to hydrotreatment catalysts with the current identified molecules. However, further works for the speciation of unknown silicon compounds must be achieved in order to be consistent with the elementary analysis. A multi technique approach including GC coupled to ICP/MS as a specific detector for silicon to improve sensitivity and selectivity and high resolution mass spectrometry to progress in the identification of unknown silicon species, and especially solutions to contamination can be proposed.

Chapitre 4. Combining FT-ICR/MS analysis and Kendrick plots for silicon speciation and molecular characterization in petroleum products at trace levels



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Combining Fourier Transform-Ion Cyclotron Resonance/Mass Spectrometry Analysis and Kendrick Plots for Silicon Speciation and Molecular Characterization in Petroleum Products at Trace Levels

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Supporting Information

ABSTRACT: A new method combining FT-ICR/MS analysis and Kendrick plots for the characterization of silicon species at trace levels in light petroleum products is presented. The method provides efficient instrumental detection limits ranging from 80 ng/kg to 5 μg/kg and reliable mass accuracy lower than 0.50 ppm for model silicon molecules in spiked gasoline. More than 3000 peaks could be detected in the *m/z* 50−500 range depending on the nature of the gasoline sample analyzed. An in-house software program was used to calculate Kendrick plots. Then, an algorithm searched, selected, and represented silicon species classes (O_2Si, O_3Si, and O_4Si classes) in Kendrick plots by incorporating model molecules' information (i.e., exact mass and intensity). This procedure allowed the complete characterization of more than 50 new silicon species with different degrees of unsaturation in petroleum products.

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4.1 Introduction

Silicon speciation has recently gained interest in the oil and gas industry due to the impact of silicon molecules on hydrotreatment catalyst performance [14]. Catalyst replacement generates important economic losses in the refining treatment [2]. To improve the refining efficiency, silicon species must be identified and quantified in order to understand the mechanisms of catalyst poisoning.

Silicon species are generally generated by antifoaming agents, such as polydimethylsiloxane (PDMS), intentionally added during the crude oil production and the refining processes to avoid emulsions [5, 30, 50]. Polydimethylsiloxane (PDMS), with a structural unit of –$(CH_3)_2SiO$- is the most employed silicon based polymer in the industry [73]. PDMS has a low surface tension and a rather good thermal stability [7], but it degrades itself around 300°C [8-10] and mainly generates siloxanes [11]. In the petroleum industry, the chemical instability of several silicon compounds [86, 90] and the possible reactivity with carbon radical at high temperatures (500-800°C), result in a wide variety of silicon species which are largely unknown. These molecules are known to affect catalyst performance [43].

Literature review on silicon poisoning reveals that silicon species can have various effects on catalyst activity depending on the nature of the catalyst [32], the molecule [49] and the experimental conditions [45]. Therefore, it seems difficult to determine the mechanistic of catalyst poisoning without a thorough estimation of the nature and amount of silicon species. This issue has been well identified but only addressed through the total determination of silicon in different products [14]. The observed concentrations ranged from about µg.kg^{-1} of Si to about mg.kg^{-1} of Si. Total silicon analysis was performed by elemental analysis mainly inductively coupled plasma atomic emission spectroscopy (ICP-OES [166]) or inductively coupled plasma mass spectrometry (ICP/MS [254]).

Recently, Chainet *et al.* [18] have identified and quantified several silicon species in naphtha and gasoline samples by GC/MS in single ion monitoring (SIM) mode. However, the selectivity of SIM mode detection does not take into account all the silicon species [18].

Several attempts to identify these silicon species using gas chromatography (GC) or liquid chromatography (LC) hyphenated to selective atomic detectors have been performed for the speciation of silicon [14, 254]. However, using a specific detection, the characterization is only based on the combination of retention time and atomic signature of the detector. Furthermore, silicon contamination originating from GC specific parts such as septa or column bleeding can take place and results in difficulties to achieve these determinations [14]. The use of high resolution mass spectrometry without any GC separation can solve these issues. It is then possible to analyze both high (*i.e.*, PDMS) and low molecular weight silicon compounds without any separation step and using a soft ionization mode [14, 263]. Siloxanes were successfully characterized by tandem mass spectrometry (MS/MS) using atmospheric pressure chemical ionization [243, 244] and electrospray (ESI) [264]. The benefits of high resolution and exact mass measurement obtained by ESI-FT-ICR/MS [249] have already been demonstrated for PDMS fragmentation patterns as molecules directly characterized by their raw formula [222, 250, 252] and with the additional abundance of silicon isotopes [253].

Combining ultra-high resolution and high mass accuracy [249], FT-ICR/MS appears to be the most attractive technique for the characterization of individual silicon species in complex matrices. However, FT-ICR/MS mass spectra of petroleum products contain several thousand of peaks [265] and the structural elucidation of these specific compounds at trace levels is not directly achievable without a specific data treatment. The implementation of Kendrick plots [266] in this case allowed a full data interpretation and efficient representation of the different classes of compounds by displaying each heteroatom content (e.g., O_3Si or O_2Si) [267].

In this work, we present a new analytical methodology for a rapid characterization of unknown silicon species at trace levels in light petroleum products such as gasoline and naphtha. Our approach is based on ESI-FT-ICR/MS analysis with the use of an home-made software which calculates the Kendrick plots. Then, a specific algorithm integrated in the software is used to search, select and represent unknown silicon species into homologous series according to alkylation, classes (numbers of heteroatoms), and types (rings plus double bonds).

4.2 Experimental Section

4.2.1 Standards and Samples

The selection of 16 commercially available model silicon compounds is based on the actual knowledge of silicon chemistry in the oil and gas industry. Different chemical families such as siloxanes (cyclic and linear), ethoxysilanes and silanols were selected (Table 4-1). These silicon compounds are used as model molecules in FT-ICR/MS analysis and are used afterwards for the direct search, selection and representation of compounds classes by applying the algorithm to Kendrick plots. The full description of the algorithm is shown in the Supporting Information section for more details (Annexe 4-Section 1).

Individual analytical standards were purchased from Sigma-Aldrich (Lyon, France) and from Interchim (Montluçon, France). Methanol and Ethanol of LC grade were obtained from Merck (Darmstadt, Germany). A standard mixture solution of 100 µg.kg^{-1} was prepared by solubilization of silicon compounds in methanol and ethanol and different dilutions were achieved to evaluate the sensitivity of the ESI-FT-ICR/MS method. Solutions and standards were stored in 30 ml high density polyethylene bottles at 4°C to avoid condensation and glasses adsorption of silicones prior usage [86]. Furthermore, extreme care was applied to the laboratory during the whole sample preparation and analysis in order to avoid contamination by personal care, cosmetic products and specific parts containing silicones (e.g. vial, septa, lubricant... [14, 203]).

The properties of the all analyzed petroleum samples were previously described by Chainet *et al.* [18]. Two naphtha samples (N1 and N2) used prior to be steam cracked (feeds) and two pyrolysis gasolines (G3 and G5) collected after the steam cracking process (end products) were analyzed by ESI-FT-ICR/MS. Gasoline A, coming from a fluid catalytic cracking process [18], without traces of silicon (previously measured by ICP/MS) was used to determine the matrix effect and the sensitivity of the method by spiking model silicon compounds after a preliminary dilution.

4.2.2 ESI-FT-ICR/MS Instrumentation

Ultra high resolution mass spectra were acquired using a LTQ-FT Ultra Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR/MS) (Thermo Fisher Scientific, Bremen, Germany) equipped with a 7 Tesla superconducting magnet and an electrospray (ESI) ion source (IonMax Thermo Fisher Scientific, Bremen, Germany). Sample solutions were injected by a syringe infusion pump at a flow rate of 5 $\mu L.min^{-1}$ in ESI positive mode.

All parameters were adjusted to obtain optimal high mass accuracy and mass resolution. The key measurement parameters for positive ESI ionization were as follows: capillary temperature, 300°C; capillary voltage, 100V; tube lens voltage, 45V; and source voltage, 5kV. According to simulated distillation analysis previously achieved for these gasoline samples, [18] the mass range was set to m/z 50-500. Mass spectral resolution of 100,000 and 200,000 at m/z 400 was performed because the latter mass resolution allowed the separation of ^{13}C and ^{29}Si isotopes from the silicon molecules and strengthens the characterization. External mass calibration was achieved with an acceptable maximum error range of 1 ppm using a solution of CalMix Proteomass for LTQ-FT-Hybrid (Supelco, Bellefonte, PA, United States). 16 or 64 µscans were accumulated and co-added prior to the Fourier transform to reduce electronic noise and to improve the signal to noise ratio of the resulting spectra. Peaks with a signal to noise ratio equal or higher than six times of the standard deviation of the baseline noise were integrated by the software designed at IFPEN and automatically generated the mass spectra and the Kendrick plots. The specific algorithm (see Supporting information for details-Annexe 4-section 1), included in this software, was applied to Kendrick plots to select and represent all compounds differing by their carbon number (homologous series), type (number of rings plus double bonds or double bond equivalent, DBE [268]) and their heteroatom content (class).

Elemental composition were assigned using Xcalibur software (Thermo Fisher Scientific, Bremen, Germany) limited to the molecular formula $C_cH_hN_nS_sO_oSi_x$ potentially present in the different petroleum samples with $0 \leq c \leq 40$, $0 \leq h \leq 200$, $0 \leq n \leq 2$, $0 \leq s \leq 2$, $0 \leq o \leq 10$ and $0 \leq x \leq 10$). According to Rodgers *et al*. [269], mass accuracy alone provides elemental composition only up to m/z 400. However, to strengthen the assignment of elemental composition for silicon species, if two (or more) elemental compositions were found within a mass tolerance of 1 ppm, one chemical formula can usually be confirmed or eliminated with the presence of ^{29}Si using a mass spectral resolution of 200,000 at m/z 400. The comparison between the D_6 mass spectrum simulation, representing the separation of ^{13}C and ^{29}Si isotopes, and the D_6 mass spectrum obtained from spiked gasoline A analysis is available from the Supporting Information section for further details (Annexe 4-Section 2-Figure A1).

4.2.3 Model molecules analysis by ESI-FT-ICR/MS and matrix effect

Silicon model molecules were analyzed by positive ion ESI-FT-ICR/MS in order to evaluate the sensitivity, the mass accuracy and the possible characterization of unknown silicon compounds. Preliminary results have been obtained in methanol with very low detection limits (LODs) ranging from 8 fg.kg^{-1} to 40 pg.kg^{-1} for 8 model silicon model molecules. However, methanol was not adapted for the solubilization of gasoline. The objective was to dissolve silicon compounds in gasoline samples and further allowed the ionization of silicon compounds at very low concentration levels. Therefore, gasoline was diluted with a 1:10 dilution in ethanol as a protic solvent and directly analyzed by ESI-FT-ICR/MS. A complete test mixture of sixteen silicon compounds (Table 4-1) was injected to calculate detection limits. All model compounds are characterized by their raw formula with a mass error below 0.5 ppm. Detection limits in ethanol are more important than in methanol but values are ranging from 2 ng.kg^{-1} to 4 µg.kg^{-1} depending on the signal response of each molecule by ESI-FT-ICR/MS. These values are useful for the detection of silicon compounds at trace levels in complex matrices.

Petroleum products appeared as one of the most complex matrices with respect to the relative number of compounds. Even if gasoline is much less complex than crude oil, this work was focused on light petroleum products (naphtha and gasoline) because silicon compounds observed at trace levels in these products induce severe problems on catalyst [14]. To evaluate the matrix effect, gasoline A was spiked with sixteen model molecules at 10 µg.kg^{-1} injected and analyzed by ESI-FT-ICR/MS after a 1:10 dilution in ethanol. The mass spectrum of spiked gasoline A with nominal mass zoom insets for H, D and B silicon compounds is presented in Figure 4-1. When using the ESI mode, nitrogen and oxygen compounds are mainly detected in gasoline A between the masses m/z 100 and 300. The three nominal mass zoom insets demonstrate the usefulness of ESI-FT-ICR/MS for the detection of silicon compounds at trace levels in a gasoline sample. In Figure 4-1, silicon compounds at 10 µg.kg^{-1} injected with signal to noise ranging from 6 to 360 are clearly separated from the rest of the hydrocarbon matrix (Table 4-1). Among the sixteen molecules injected at 10 µg.kg^{-1} in gasoline A, thirteen silicon model molecules are clearly characterized by their exact masses. Table 4-1 presents silicon model species characterized in spiked gasoline A and reports specifically detection limits and the mass accuracy of the ESI-FT-ICR/MS method.

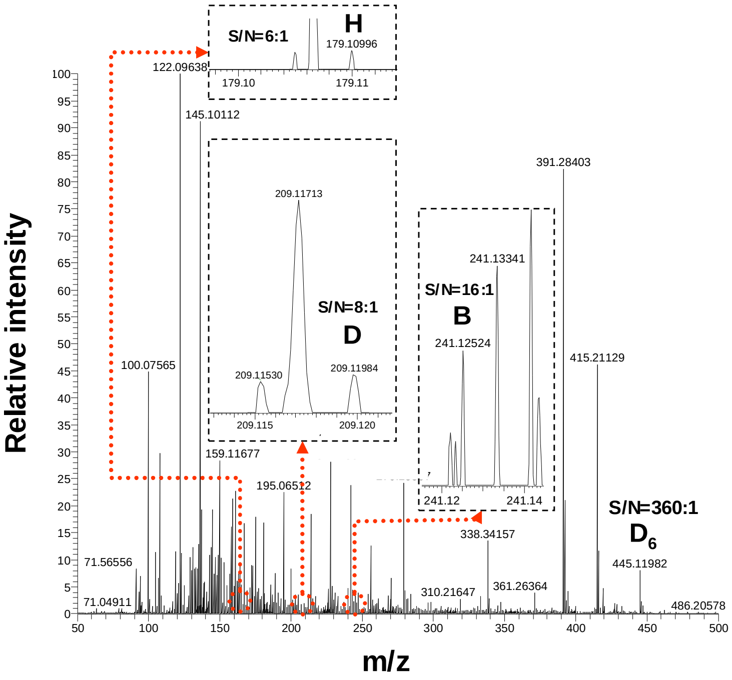


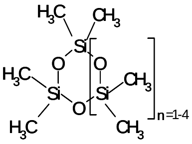
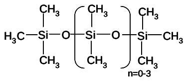
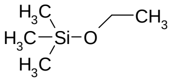
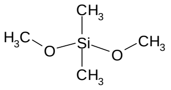
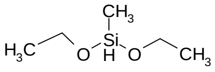
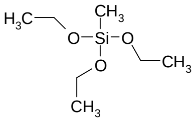
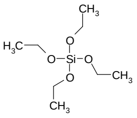
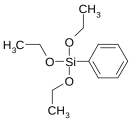
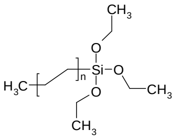
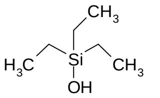
Figure 4-1. Total mass spectrum of all detected compounds with three nominal mass zoom insets for H, B and D silicon species at 10 µg.kg^{-1} injected in spiked gasoline A and (b) extracted mass spectrum of the 13 silicon species spiked obtained with an ESI-FT-ICR/MS acquisition (64 µscans and resolution of 200,000 at m/z 400). All silicon compounds characterized in spiked gasoline A are listed in Table 4-1

Efficient instrumental detection limits ranging from 80 ng.kg^{-1} to 5 µg.kg^{-1} and a reliable mass accuracy below 0.52 ppm for all silicon model molecules are obtained in gasoline A. Only three linear siloxanes L_2-L_4 cannot be identified in the spiked gasoline due to their low signal response. However, these molecules can be detected using the "Narrow SIM mode" which consists of focusing the mass spectrum acquisition on a small mass range (typically ± m/z 30) [270]. As previously observed in ethanol, various response factors are obtained for the different molecules (Figure 4-1 and Table 4-1). For instance, the relative intensity of dodecamethylcyclohexasiloxane (D_6) is 61 times higher than that of dimethoxydimethylsilane

(DEMS). Basically, this low signal response may be due to the volatility of several silicon species or to the chemical structure of the molecule (Table 4-1). Detection limits were in the lower end of the range of values previously published in the literature for these molecules [14, 18]. The ESI-FT-ICR/MS displayed a very high sensitivity for these compounds, with a sufficient resolution and a reliable mass accuracy allowing access to trace level detection of silicon model molecules in complex matrices such as petroleum products.

The number of peaks detected in an ultrahigh resolution mass spectrum of gasoline (around 3,000 isotopes included in gasoline A) is quite substantial (Figure 4-1) and makes the characterization of unknown molecules at trace levels very hard to be achieved manually. To overcome this analytical challenge, the developed algorithm was performed to obtain Kendrick plots for a compact visual display of mass spectra [266, 267] and a powerful representation of compounds by alkylation, types and classes in complex matrices.

Table 4-1. List of silicon molecules with their abbreviation, boiling point, mass, relative intensity, mass error, detection limits (LOD), Kendrick mass defect (KMD), formula $[M+H]^+$ and chemical structure of silicon model molecules injected at 10 µg.kg^{-1} in spiked gasoline obtained with an ESI-FT-ICR/MS acquisition (64 µscans and resolution of 200,000 at m/z 400)

Molecule	BP °C	Measd mass	Theor mass	error ppm	I_r	LOD µg.kg^{-1}	KMD	Structure
Cyclic siloxanes								
Hexamethylcyclotrisiloxane (D$_3$) $C_6H_{18}O_3Si_3$	134	223.06355	223.06365	0.10	9.28	1	0.185	
Octamethylcyclotetrasiloxane (D$_4$) $C_8H_{24}O_4Si_4$	175	297.08227	297.08244	-0.17	4.70	1	0.249	
Decamethylcyclopentasiloxane (D$_5$) $C_{10}H_{30}O_5Si_5$	211	371.10114	371.10123	-0.25	9.89	1	0.313	
Dodecamethylcyclohexasiloxane (D$_6$) $C_{12}H_{36}O_6Si_6$	245	445.11982	445.12002	-0.2	61.32	0.08	0.377	
Linear siloxanes								
Hexamethyldisiloxane (L$_2$) $C_6H_{18}O\ Si_2$	100	n.d.	163.09676	--	--	--	0.085	
Octamethyltrisiloxane (L$_3$) $C_8H_{24}O_2Si_3$	153	n.d.	237.11214	--	--	--	0.152	
Decamethyltetrasiloxane (L$_4$) $C_{10}H_{30}O_3Si_4$	194	n.d.	311.13448	--	--	--	0.213	
Dodecamethylpentasiloxane (L$_5$) $C_{12}H_{36}O_4Si_5$	210	385.15310	385.15327	-0.44	2.41	2	0.277	
Ethoxysilanes								
Ethoxytrimethylsilane (I) $C_5H_{14}O\ Si$	75	119.08865	119.08867	-0.17	1.01	5	0.044	
Dimethoxydimethylsilane (DMDS) $C_4H_{12}O_2Si$	81	121.06792	121.06793	-0.08	1.05	5	0.067	
Diethoxymethylsilane (DEMS) $C_5H_{14}O_2Si$	94	135.08306	135.08358	-0.50	1.00	5	0.067	
Triethoxymethylsilane (H) $C_7H_{18}O_3Si$	143	179.10996	179.10980	0.16	1.06	5	0.090	
Tetraethoxysilane (D) $C_8H_{20}O_4Si$	168	209.11984	209.12036	-0.50	1.24	4	0.112	
Phenyltriethoxysilane (B) $C_{12}H_{20}O_3Si$	265	241.12524	241.12545	-0.21	2.69	2	0.143	
Triethoxyoctylsilane (C) $C_{14}H_{32}O_3Si$	168	277.21921	277.21935	-0.13	4.54	1	0.090	 n=6
Silanol								
Triethylsilanol (TES) $C_6H_{16}O\ Si$	158	133.10467	133.10432	0.35	1.23	4	0.044	

4.2.4 FT-ICR/MS characterization and Kendrick plots

The aim of the software algorithm, based on Matlab routine, is to improve both the exploitation and interpretation of FT-ICR/MS mass spectra of petroleum products in the laboratory. It is specifically used for class search, selection and representation (O_2Si, O_3Si, O_4Si) by the application of a specific algorithm. In our method, this algorithm was directly applied to FT-ICR/MS data of gasoline samples and silicon model molecules used as references (Table 4-1). This application results in the characterization of unknown silicon compounds displayed by alkylation, type and class on the Kendrick plots.

From the data obtained by ultra-high resolution mass spectrometry, an elemental composition ($C_cH_hN_nS_sO_oSi_x$) can be calculated within the different elements previously defined. For hydrocarbon matrices, a specific mass scale based on the repeating CH_2 mass was developed [266] and successfully applied to ultrahigh resolution mass spectra [267, 271-275]. Thus, it is then possible to identify a series of compounds with the same number of unsaturations defined as homologous series, with different extents of alkylation following Equation 4-1.

$$\mathbf{Kendrick\ mass = (IUPAC\ mass) \times \frac{14}{14.01565}}$$

Equation 4-1. Normalization of the Kendrick mass

With the Kendrick mass scale, members of a homologous series (namely, compounds with the same heteroatom composition and identical number of rings plus double bonds, but different numbers of CH_2 groups) will have identical Kendrick mass defect (KMD), defined in Equation 4-2 [267]. For the same heteroatom content or class (O_2Si) but different number of unsaturations (type), the Kendrick mass defect changes and the different homologous series are separated by 0.01340 Da corresponding to the Kendrick mass defect of two hydrogens. Similarly, the Kendrick mass defect for compounds of a given class will be displaced vertically from those of other classes such as O_2Si, O_3Si, or O_4Si (Figure 4-2).

$$\mathbf{KMD = (exact\ Kendrick\ mass - nominal\ Kendrick\ mass)}$$

Equation 4-2. Kendrick mass defect calculation

For each analyzed sample by ESI-FT-ICR/MS, silicon model molecules measured masses were added in each Excel worksheet containing the raw data samples and were normalized to the highest detected peak. This peak was the reference peak used for the normalization since the routine began with the highest detected peak. The software then calculated all Kendrick mass defects (Table 4-1) which were plotted against Kendrick mass. This allowed generating the Kendrick plot of real samples also containing model molecules data which were added for reference. Then, the specific algorithm was applied to silicon model molecules displayed in the Kendrick plot. This algorithm (see Supporting Information for details-Annexe 4-Section 1) allowed the selection and the representation of silicon compound classes based on the previously added reference molecules in the Excel worksheet. Finally, unknown silicon molecules with different carbon (homologous series) and type (different number of DBE) than model molecules but belonging to the same class were displayed in the Kendrick plot.

Figure 4-2 illustrates the Kendrick plot of the sixteen model silicon molecules displayed in the different classes of interest. Cyclic (D_3-D_6) and linear siloxanes (L_2-L_5) are displayed on a straight line and are separated by the exact repeating mass of 74.0188 Da (74 Da in Kendrick mass scale) for C_2H_6OSi group. According to this repeated mass (e.g. 74. Da) between siloxanes and the reliable mass accuracy of FT/MS, this method easily allows the characterization of siloxanes with higher molecular mass. An example for tetradecamethylhexasiloxane (L_6), not initially included in the test mixture, is illustrated in Figure 4-2. On the contrary, several model compounds, more specifically ethoxysilanes, have the same Kendrick mass defect (Table 4-1 and Figure 4-2). They belong to the same homologous series of the class. Molecules I and TES have a KMD of 0.044 Da and are classified into O_1Si class. DMDS and DEMS have a KMD of 0.067 Da and are classified into O_2Si class. These compounds are respectively separated two by two by the repeating mass CH_2 (14 Da in Kendrick mass). However, I and TES differed by a CH_2 group but they do not belong to the same chemical family (ethoxysilane and silanol respectively). Thus, a similar raw formula can be assigned to several developed chemical structures. Ethoxysilanes H and C have a KMD of 0.090 Da and can be classified into O_3Si class. These compounds are separated by a mass difference of 98 Da in Kendrick mass scale, which represents a difference of seven carbons. For O_4Si class, only tetraethoxysilane (D) is present in the test mixture but the software algorithm only needs the Kendrick mass of one compound per class to obtain other unknown silicon molecules belonging to O_4Si class.

The combination between ESI-FT-ICR/MS analysis (great sensitivity, high mass accuracy and resolution) and Kendrick plots will be applied to highlight the occurrence of new silicon species in light petroleum products.

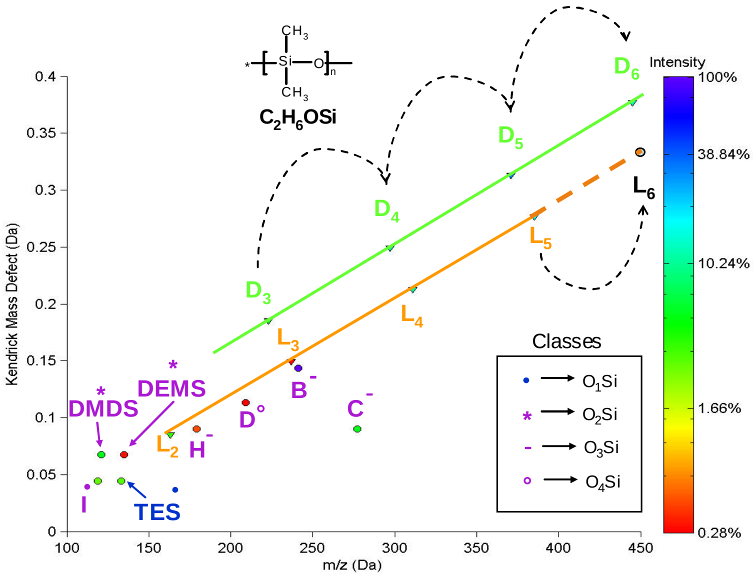


Figure 4-2. Kendrick plot of 16 standard silicon molecules (100 µg.kg^{-1} injected in ethanol) obtained with an ESI-FT-ICR/MS acquisition (64 µscans and resolution of 200,000 at m/z 400). This plot represents horizontally model silicon species according to their Kendrick mass (number of carbon) and vertically to their Kendrick mass defect (double bond equivalent). Cyclic and linear siloxanes are displayed on a straight line with the same repeating mass (C_2H_6OSi). All Kendrick mass defects are listed in Table 4-1

4.3 Results and Discussion

Four samples originating from a steam cracking process were analyzed by ESI-FT-ICR/MS after a 1:10 dilution in ethanol to look for silicon model molecules and more specifically unknown silicon species. For further information, the mass spectrum and the Kendrick plot of a gasoline are available in Annexe 4-Section 3-Figure A3.

4.3.1 Characterization of known silicon species in real samples

The six model molecules used as reference (cyclic siloxanes (D_3-D_6), triethoxysilane (H, O_3Si family) and tetraethoxysilane (D, O_4Si family) are characterized in the different samples (Annexe 4-Section 4-Table A1). The characterization of these molecules is performed after the comparison of silicon model molecules spiked in gasoline sample A (Table 4-1). Mass error below 0.20 ppm is obtained for all detected model compounds in these samples and confirms the mass accuracy of the ESI-FT-ICR/MS. Cyclic siloxanes (D_n) are obtained by a straight line generated and separated by the repeating mass of m/z 74 (C_2H_6OSi), as previously indicated in Figure 4-1 for silicon model molecules. Triethoxysilane (H) and tetraethoxysilane (D) are respectively characterized in the light naphtha samples 1 and 2 (Figure 4-3a and Figure 4-3b) and in all investigated samples (Annexe 4-Section 4-Table A1).

Cyclic siloxanes are directly coming from PDMS degradation following a depolymerization mechanism which has been well-established in the literature [8, 9, 11].

Cyclic siloxanes (D_n) have been also quantified by GC/MS SIM in other petroleum products [18]. In this case, the total silicon content does not match with the silicon species characterized and a significant difference between the total silicon content and the sum of silicon species detected is observed. This highlights the fact that a wide array of other non-detected silicon species could be observed. The wide array of unidentified silicon species suggests that a large set of rearrangement reactions between other silicon molecules and hydrocarbon radicals could occur in petroleum products and generate other unknown silicon molecules potentially affecting catalysts. Camino *et al.* [11] have also demonstrated the presence of rearranged oligomeric siloxanes compounds during thermal degradation of PDMS under N_2 and at 800°C (steam cracking temperature). The oxidation conditions occurring during PDMS degradation could generate ethoxysilane species such as H and D [10]. When dealing with catalysis studies, the reactivity between tetraethoxysilane (D) and alumina surface was studied in the presence of water at high temperature similar to that the ones occuring in the steam cracking process [56]. No clear effect in poisoning was highlighted but silanols groups were formed on alumina.

The current characterized silicon molecules have no significant effect on the hydrotreatment catalysts. These results suggest that the poisoning of catalysts is certainly due to other unknown silicon species.

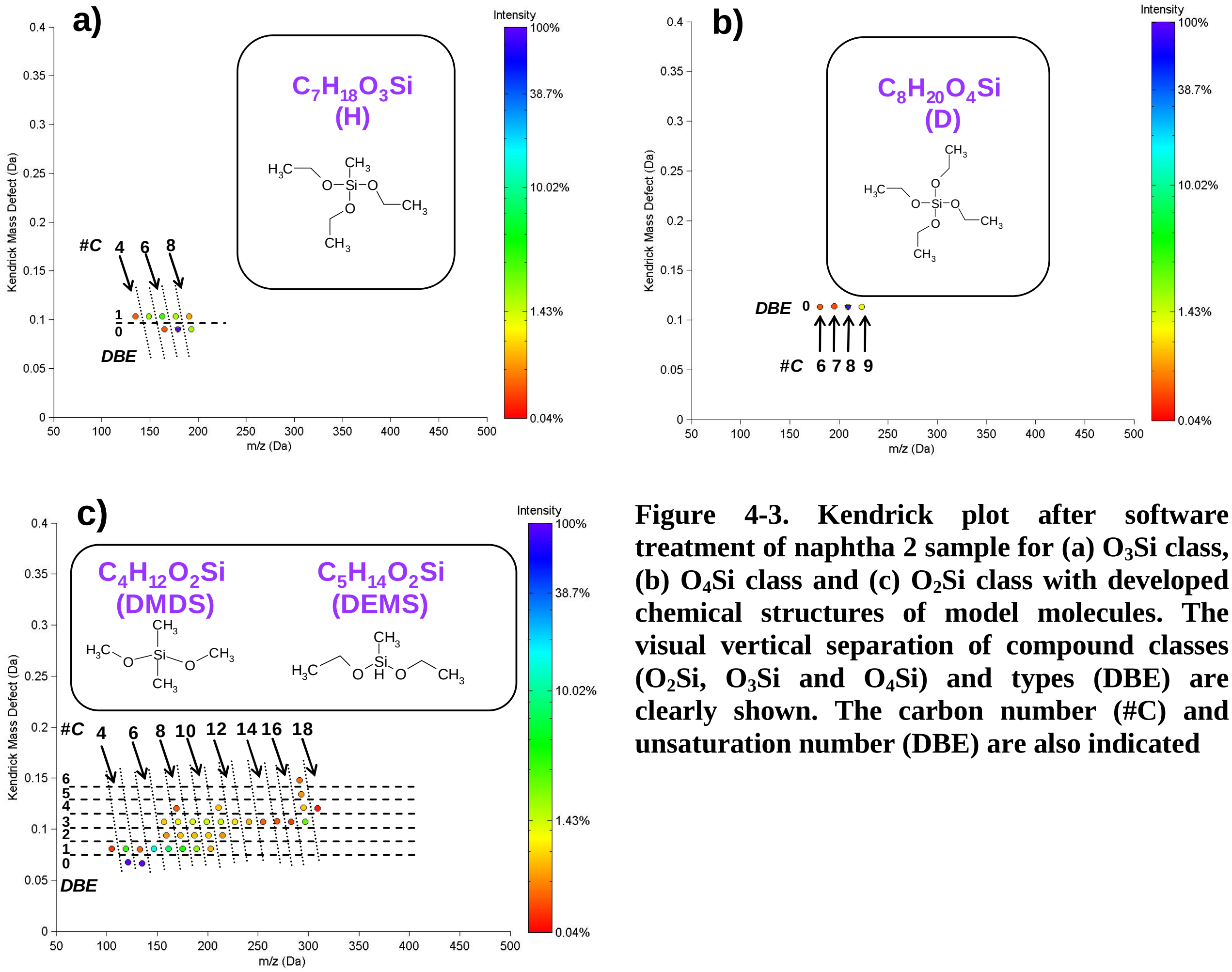


Figure 4-3. Kendrick plot after software treatment of naphtha 2 sample for (a) O_3Si class, (b) O_4Si class and (c) O_2Si class with developed chemical structures of model molecules. The visual vertical separation of compound classes (O_2Si, O_3Si and O_4Si) and types (DBE) are clearly shown. The carbon number (#C) and unsaturation number (DBE) are also indicated

4.3.2 Kendrick plots and application of the method to real samples

According to the software algorithm applied to model molecules (Figure 4-3), our characterization method was able to recognize silicon molecules at trace levels in complex matrices. Kendrick plots are calculated for all investigated samples but only the results for naphtha 2 are illustrated in Figure 4-3 due to the large number of characterized silicon species. Compounds of the same homologous series but with a different number of CH_2 units will align on a single horizontal line. Species are separated by 14 Da and have identical Kendrick mass defect. Similarly, molecules belonging to the same class but with different unsaturation number (differing by H_2) will align on horizontal lines separated by the Kendrick mass defect of two hydrogens equal to 0.01340 (Figure 4-3). Among the 4919 detected peaks in naphtha 2, 41 molecules are characterized and classified in O_2Si, O_3Si and O_4Si classes and most of these probably consisted of an ethoxysilane group. 96% of the silicon molecules are characterized by their raw formula with a mass error range below 0.50 ppm in these samples (Annexe 4-Section 4-Table A1). This table also includes silicon molecules contained in other samples investigated than naphtha 2. The model molecules DMDS and DEMS are used for the characterization of the O_2Si class (Figure 4-3c). The Kendrick plot illustrates seven homologous series of O_2Si class (included DMDS and DEMS as model molecules) containing molecules from C_3 to C_{18} and with a number of unsaturations ranging from zero to six (Figure 4-3c). The same method was applied to H (O_3Si class) and D (O_4Si class) model molecules. As previously mentioned, these two molecules are characterized in real samples, respectively for O_3Si and O_4Si classes (Figure 4-3a-b). Moreover, the method highlights the presence of two homologous series of O_3Si species ranging from C_4 to C_8, with zero and one unsaturation (Figure 4-3a) and one homologous series of O_4Si class with carbon number between C_6 to C_9 but without unsaturation (Figure 4-3b) in naphtha 2. The presence of silicon compounds with unsaturations (O_2Si and O_3Si classes) is a useful and novel information for catalyst studies. In fact, silicon species with unsaturations are more reactive and can severely affect catalysts [276, 277]. To our knowledge, these types of molecules had never been characterized before in petroleum products.

The different classes of silicon species in all samples are presented in Figure 4-4. More than 50 new different silicon species are characterized in this work. The O_2Si class is the most important with more than 30 characterized species. Concerning the naphtha 1, similar species to naphtha 2 are characterized. In fact, the O_2Si and O_3Si species are displayed in two homologous series with one and two unsaturations respectively, ranging from C_3 to C_{10} and from C_2 to C_9 (Annexe 4-Section 4-Table A1). The O_4Si species contained in naphtha 1 range between C_6 and C_{10} without any unsaturation.

These results showed that silicon species in naphtha samples have approximately the same chemical nature and only differ by the number of characterized compounds. On the contrary, the number of silicon species belonging to the previous families substantially decreases in the gasoline samples. Nevertheless, tetraethoxysilane is also characterized in all analyzed samples. This result confirms that there is no matrix effect between naphtha and gasoline samples for this type of molecules. Silicon (such as tetraethoxysilane) or silicon-sulfur additives are intentionally added during hydrocarbon steam cracking to avoid coke formation and probably explain the presence of this molecule [40]. However, this type of compound could be also originated from PDMS thermal degradation with a reaction between silicon molecules and carbon radicals [10, 11].

Knowledge of these new classes of silicon molecules is essential to progress in silicon speciation in petroleum products. However, quantitative analysis of silicon molecules is not possible by ESI-FT-ICR/MS in our case due to the presence of unknown silicon species with different response coefficients. For a complete characterization and quantification, commercially available or synthesized molecules are still necessary. Therefore, hyphenated techniques (GC-ICP/MS or GC/MS in SIM mode) as complementary techniques to FT-ICR/MS must be used.

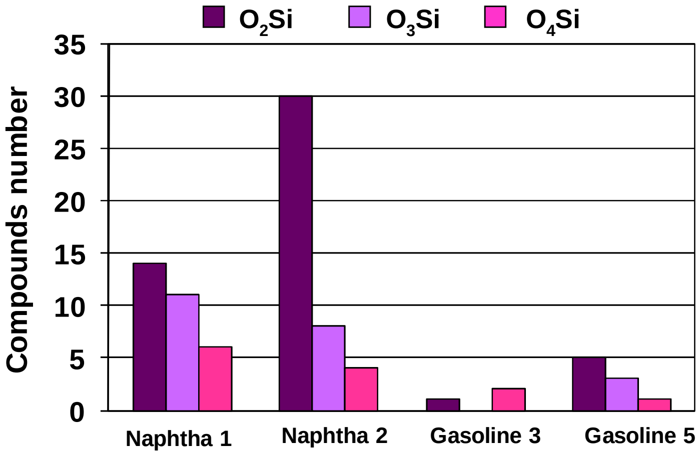


Figure 4-4. Species distribution for O_2Si, O_3Si and O_4Si classes in all investigated samples

4.4 Conclusions

Previous studies using hyphenated techniques have allowed the characterization of several silicon molecules but quantification results were not in total agreement with elemental analysis highlighting that numerous unknown silicon species are still present.

In this paper, a rapid and novel method based on ESI-FT-ICR/MS analysis combined to Kendrick plots was developed for the characterization of unknown silicon species at trace levels. The use of a specific algorithm integrated in an homemade software facilitates the automatic search, selection and representation of classes in Kendrick plots. These results confirm the occurrence of several silicon molecules, specifically cyclic siloxanes (previously quantified by GC/MS SIM) but also show the presence of more than 50 new silicon species which have not been yet characterized. Most of these molecules appear to be ethoxysilanes and are classified in chemical classes (O_2Si, O_3Si and O_4Si) with different carbon number (C_2-C_{18}) and unsaturations ranging from zero to six. Homologous series of new silicon molecules with unsaturations are characterized for the first time in petroleum products using a combined approach of model molecules ESI-FT-ICR/MS analysis with Kendrick plots. This new information is essential for further catalysis studies including more reactive silicon molecules with several unsaturations.

Chapitre 5. Complementary approach between GC-ICP/MS and GC-GC/TOFMS for silicon speciation in light petroleum samples

5.1 Towards silicon speciation in light petroleum products using gas chromatography coupled to inductively coupled plasma mass spectrometry (GC-ICP/MS) equipped with a dynamic reaction cell (DRC)

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5.1.1 Abstract

Silicon speciation has recently gained interest in the oil and gas industry due to the important poisoning problems caused by silicon on hydrotreatment (HDT) catalysts. To limit the poisoning of catalyst, several solutions can be envisaged in the oil and gas industry such as trapping of these compounds before the catalytic units or increasing the resistivity of the catalysts. The poisoning effect clearly depends on the silicon molecule. Thus, the chemical structure of silicon species must be determined before developing these solutions. The hyphenation of gas chromatography (GC) coupled to inductively coupled plasma mass spectrometry (ICP/MS) allowed a specific detection to determine the retention times of all silicon species. The optimization of the dynamic reaction cell (DRC) of the ICP/MS using hydrogen as reactant gas successfully demonstrated the resolution of the interferences ($^{14}N^{14}N^+$ and $^{12}C^{16}O^+$) initially present on ^{28}Si without the use of this system. The linearity appeared as excellent for silicon compounds and instrumental detection limits were ranged from 20 to 140 µg of Si.kg^{-1}. A continuous release of silicon in the torch was suspected probably due to the use of a torch and an injector made of quartz. A non universal response for silicon was observed and it was clearly necessary to use response coefficients to quantify silicon compounds. However, the main aim of this work was to determine the retention times of unknown silicon species to further allow their characterization by GC-GC/TOFMS in order

to determine their chemical structure. Known silicon compounds such as trimethylsilanol (TMSOH) and cyclic siloxanes (D_3-D_7) coming from the PDMS degradation were confirmed. More than 15 new silicon species were characterized in PDMS degradation samples produced under thermal cracking of hydrocarbons and more than 10 species were characterized in real gasoline samples coming from different refinery processes. These results clearly demonstrated the presence of new silicon compounds never characterized in the literature and are soon to be characterized using a powerful three dimensional system GC-GC/TOFMS to obtain their chemical structure. This information was crucial to limit the poisoning effect of catalysts by silicon in the oil and gas industry.

5.1.2 Introduction

Silicon is known to severely affect the performance of hydrotreatment catalysts and considerably reduce their life time [2]. Silicon species were adsorbed at the surface of the catalytic system. They induced a decrease of the activity and caused its replacement which represents a great economic loss. The chemical structure of silicon compounds appeared as crucial beacuse of the different effects on catalyst [49]. For these reasons, silicon speciation must be achieved to identify and quantify silicon species in hydrotreatment feeds to limit their poisoning effect [14]. The ultimate aim is then to trap silicon compounds before the catalytic systems or to understand the poisoning mechanism in order to increase the resistivity of the catalysts against silicon.

Silicon compounds come from the degradation of polydimethylsiloxane (PDMS) added as antifoaming agents during refining processes such as distillation, coking, visbreaking or steam cracking and also during crude oil recovery [4, 5, 7]. Due to the initial injection of PDMS generally around 50 $mg.kg^{-1}$, silicon compounds are produced at trace levels in petroleum products. Total silicon content can be measured by ICP-OES [278] and by ICP/MS [254]. The concentrations generally reported range from several hundred µg of $Si.kg^{-1}$ and several mg of $Si.kg^{-1}$ in petroleum products [14]. Up to now in the oil and gas industry, cyclic siloxanes (D_n) with traces of tetraethoxysilane and decamethylpentasiloxane (L_5) were identified and quantified using GC/MS SIM (single ion monitoring) in naphtha and gasoline samples [18]. However, comparising total silicon content obtained by GC/MS SIM and by ICP-OES, around 50% of the silicon species were quantified. A wide array of other silicon species is therefore present in these products. These compounds could be coming from the reaction of PDMS degradation products with carbon radicals which would increase the difficulty to analyse these molecules [14]. Using a ESI-FT-ICR/MS method combining to Kendrick plots, new silicon compounds have been characterized by their raw formula and double bond equivalent (DBE) but the chemical structure could not be determined due to the important number of possible isomers [279]. Considering the trace silicon concentration and the wide array of unknown silicon compounds, the hyphenation of GC with a sensitive and specific detection such as inductively coupled plasma mass spectrometry (ICP/MS) for silicon speciation was investigated [14].

In addition to the contamination problems during the analysis of silicon compounds, the use of GC-ICP/MS for silicon speciation appears as a great analytical challenge due to the spectral interferences at m/z 28 [14]. For the major isotope ^{28}Si (m/z 27.97638), the main interferences concerned are $^{14}N^{14}N^+$ (m/z 28.00560) and especially $^{12}C^{16}O^+$ (m/z 27.99437) for an organic matrix [136]. The presence of carbon and oxygen due to cones clogging caused the formation of $^{12}C^{16}O^+$ and limited the sensitivity of the technique due to the importance of the background signal [280]. To resolve these interferences, Pohl *et al.* [254] and Elder *et al.* [227] used ICP/HRMS respectively coupled with µSEC columns to study the analysis of silicon in crude oils and with GC for the detection of sylilated alcools. With a resolution more than R=1560 [170], the signal of silicon could be easily monitored. The use of an ICP/MS equipped with a dynamic reaction cell (DRC) appeared as a powerful tool to resolve the interferences. The principle is based on the reaction of the interferences with a reactant gas (H_2, NH_3, O_2, CH_4) at low flow rate to shift their ions detection but without affecting the signal of the investigated analyte [281, 282]. Liu *et al.* [135] have carried out experiments with NH_3 gas using ICP/MS equipped with a DRC to determine silicon traces in steels. However, others workers [283, 284] have demonstrated that the use of NH_3 for silicon did not completely resolve the interferences. In fact, a reaction between Si^+ and NH_3 formed another $SiNH_2^+$ ion (m/z 44) and considerably reduced the signal on ^{28}Si. Thus, NH_3 was not the most adapted reactant gas for silicon.

In this work, we present the development of a method for silicon speciation in petroleum products using GC-ICP/MS equipped with a dynamic reaction cell (DRC). The aim of this work is to determine the retention times of unknown silicon compounds in the investigated samples and to further allow their characterization by GC-GC/TOFMS to determine their chemical structure. First ICP/MS studies were carried out using hydrogen (H_2) as reactant gas and allowed to successfully detect total silicon in xylene matrices with a complete resolution of interferences [29, 285]. After the DRCoptimization on three silicon model molecules in acetone using GC-ICP/MS, the analytical performances of the method were presented in terms of detection limits and linearity. The matrix effect was also evaluated in spiked gasoline. Several samples coming from the production on a pilot plant used to degrade PDMS under thermal cracking of hydrocarbons and real samples taken from different refinery processes were analyzed by GC-ICP/MS.

5.1.3 Materials and Methods

5.1.3.1 Silicon standards and solutions

According to previous silicon speciation studies [18, 279], a representative mixture of 30 commercially available silicon standard molecules potentially, coming from the thermal degradation of PDMS, was used in this work. Individual standards of silicon compounds were purchased from Sigma-Aldrich (Lyon, France) and from Interchim (Montluçon, France). A mixture of these silicon compounds was prepared in acetone at a concentration of 1 mg.kg^{-1} and then was injected in GC-ICP/MS. Different dilutions were achieved to calculate the detection limits and to study the linearity of the method. Using GC-ICP/MS, the identification of the molecules is based on the retention times of model silicon species. The complete analytical procedure for the storage and the injection of samples to avoid contaminations was previously reported in Chainet *et al.* [18]. The raw formula, boiling points, molecular masses and the chemical structure of silicon compounds are indicated in Annexe 5, but are also reported in Chainet *et al.* [18, 279].

5.1.3.2 Samples and storage

Two different types of samples were investigated in this work. Firstly, various real naphtha and gasoline samples coming from different refinery processes were supplied by AXENS (Rueil Malmaison, France). The boiling range and the concentration in total silicon of these different samples are indicated in Table 5-1. These samples were stored at 4°C in the refrigerator during several months similarly to the current storage applied to silicon speciation. However, silicon species can be modified between the sampling and the analysis.

Table 5-1. List of the investigated samples coming from different refinery processes

Samples	Cuts	Refinery process	Boiling range	Concentration (mg of Si.kg^{-1})
FCC	gasoline	FCC	10→197	<5 µg.kg^{-1} (ICP/MS)
S7578	naphtha	coking	-6→208	1.50±0.07
6457	gasoline	hydrogenation	77→242	2.70±0.10
6458	gasoline (toluene cut)	hydrogenation	102→131	4.50±0.10
N1	naphtha	steam cracking	37→177	0.53±0.04
N2	naphtha	steam cracking	38→181	0.56±0.02
G3	gasoline	steam cracking	23→226	1.02±0.08
G5	gasoline	steam cracking	23→250	2.53±0.10

To avoid this evolution during this period of storage, fresh PDMS degradation samples were produced using a pilot plant to obtain representative conditions of the degradation of an antifoaming under thermal cracking of hydrocarbons. The operating conditions of the PDMS degradation tests are indicated in Table 5-2. Further details were provided in Chainet *et al.* [286] for the production of the samples and especially for the storage of the samples.

After the production of the samples, the liquid fraction was respectively stored in liquid nitrogen at -195°C and in the refrigerator at 4°C to further allowed GC-ICP/MS analysis after the production of these samples avoiding the evolution of silicon species [286].

Table 5-2. Operating conditions of the process for all produced samples [286]

Tests	Temperature (°C)	Residence time (s)	Steam (%m)	Concentration (mg.kg^{-1} of Si)
A	250	long (5.50 s)	0%	1164±70
B	500	short (0.64 s)	50%	2482±155
C	500	short (0.49 s)	13%	1342±53
D	500	long (3.48 s)	10%	1571±48
E	500	long (3.50 s)	0%	1129±83

After the optimization of the GC-ICP/MS conditions, the samples were injected after dilution in acetone depending on the total silicon concentration of the samples (Table 5-1 and Table 5-2). In this section, only the PDMS degradation effluents stored in liquid nitrogen were taken into account. The comparison of the results between PDMS degradation samples stored at 4°C and PDMS degradation samples stored at -195°C will be presented in future works to evaluate this potential evolution.

5.1.3.3 GC-ICP/MS apparatus

The GC-ICP/MS setup consisted of a Clarus 680 gas chromatograph with an ICP/MS Elan DRC II (Perkin Elmer, Waltham, Massachusetts, United States) (Figure 5-1-a). A volume of 1 µL in splitless mode was injected at 200°C through the Merlin microseal septum (Merlin Instrument Company, Half Moon Bay, CA, United States) and with a constant helium flow at 1.3 ml.min^{-1}. The separation was performed using the same low bleed capillary column DB-5 MS UI (30mx0.25 mm i.d., 0.25 µm film thickness) from J&W Scientific (Folsom, California, United States) as previously used by GC/MS [18] and by GC-GC/TOFMS [287]. The column oven temperature was programmed from 30°C (7 min) to 50°C at 2°C.min^{-1}, then to 60°C at 1°C.min^{-1}, then increased to 120°C at 2°C.min^{-1} and followed by a final temperature ramp of 10°C.min^{-1} to 280°C and held for 2 min. The total time for a run was 75 min.

The capillary column was connected to a 0.25 mm i.d. de-activated fused silica with a capillary transfer through the flexible transfer line heated at 250°C and further through a 10 cm rigid transfer line until the GC injector linked up to the ICP/MS torch (Figure 5-1-b). The injector (1.2 mm i.d.) and the torch are made of quartz. A make up gas of Argon (700 ml.min^{-1}) was added using a mass flow controller via a T-piece (Figure 5-1-b). A plasma power of 1300 W was selected after optimisation of the signal to background ratio on ^{28}Si and to obtain a robust plasma for the analysis of petroleum products. The ICP was operated with a gas flow rates of argon: 15 l.min^{-1} plasma gas and 0.6 l.min^{-1} nebulisation gas. Oxygen was added to the auxiliary argon gas at a rate of 25 ml.min^{-1} in order to minimize carbon deposition (due to the organic solvent injected on the chromatographic column) on the ICP cones.

The ICP/MS conditions were optimized using the continuous signal of the ^{128}Xe isotope. This signal served to tune the MS spectrometer, to adjust the position of the transfer line (fused silica capillary) in the torch and to optimize ICP operating parameters. These parameters were checked and optimized daily with the objective of reaching the maximum sensitivity for the ^{128}Xe isotope. Initially, the isotopes ^{28}Si ^{29}Si ^{30}Si, ^{53}Cr were respectively monitored for silicon element and for the carbon detection (^{40}Ar^{13}C) with a dwell time of 30 ms. To improve the sensitivity, the dwell time (scanning time on each point measured for the m/z monitored) was increased at 400 ms and only ^{28}Si was monitored during the analysis.

The ICP/MS detection allowed selectivity and sensitivity but several matrix interferences could be present especially at m/z 28 in organic products such as gasolines. The expected polyatomic ions affecting the detection of silicon at the most abundant isotope ^{28}Si (m/z 27.97638) are ^{12}C^{16}O (m/z 27.99437) and ^{14}N$_2$ (m/z 28.00560) [136]. In organic matrix such as gasoline, the main interference consists in the formation of CO due to the continuous injection of carbon in the plasma. To resolve interferences on the ^{28}Si, the instrument was operated using the dynamic collision-reaction cell (DRC) with hydrogen as reactant gas at 2.0 ml/min after optimization with silicon standards.

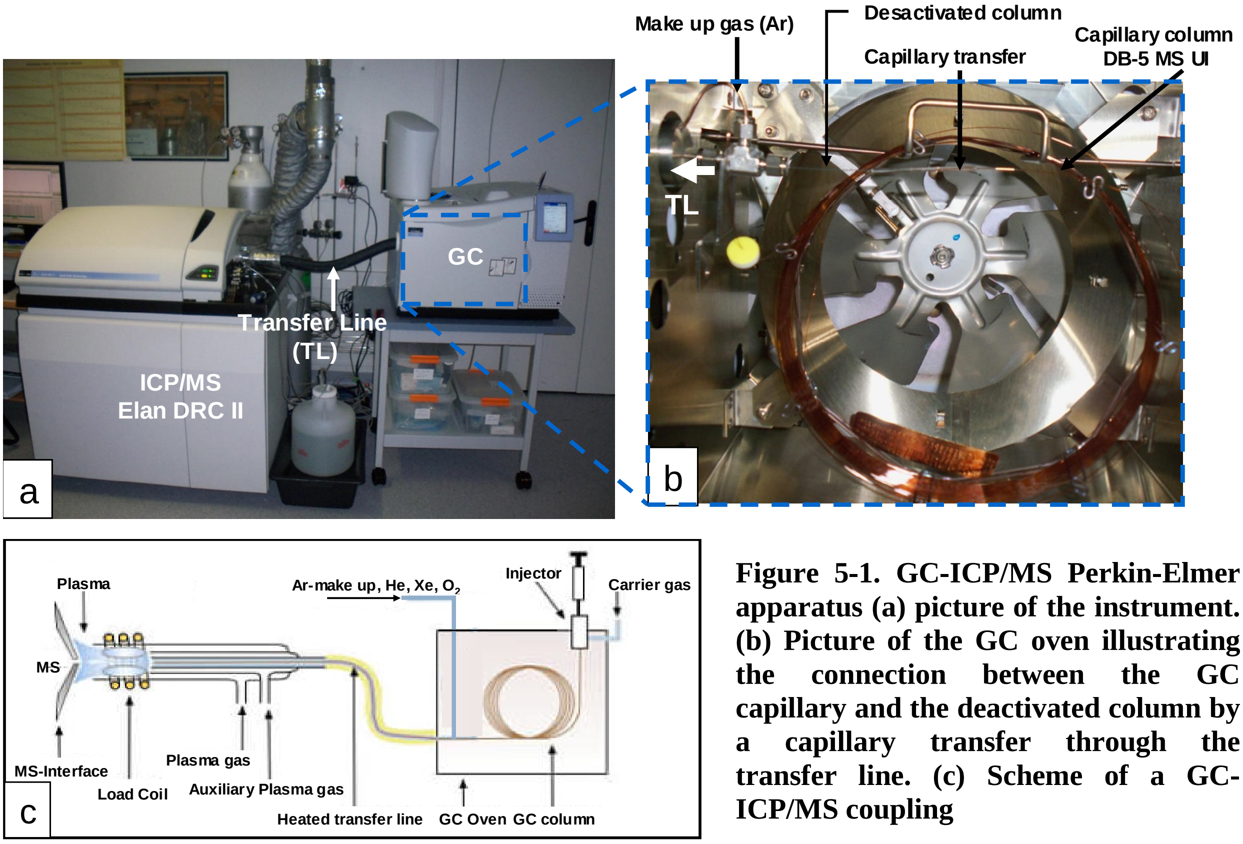


Figure 5-1. GC-ICP/MS Perkin-Elmer apparatus (a) picture of the instrument. (b) Picture of the GC oven illustrating the connection between the GC capillary and the deactivated column by a capillary transfer through the transfer line. (c) Scheme of a GC-ICP/MS coupling

5.1.4 Results and Discussion

The GC-ICP/MS was first operated without the DRC to check the GC-ICP/MS coupling. Due to the interferences on ^{28}Si, the use of the DRC appeared as crucial to be able to detect silicon compounds in a petroleum product. After the optimization step using silicon model molecules with hydrogen as reactant gas, the detection limits and the linearity were evaluated.

5.1.4.1 Optimization of the GC-ICP/MS method

5.1.4.1.1 Experiments without the DRC

The test mixture was first injected using GC-ICP/MS to test the feasibility of the coupling and to optimize the distance between the end of the GC transfer line and the injector. A good chromatographic separation was obtained but the sensitivity was not optimal due to the deposition of graphite carbon on the cones of the ICP/MS. The O_2 gas flow was then optimized to obtain appropriate conditions for silicon detection.

The test mixture of silicon compounds at 1 mg.kg^{-1} was injected by GC-ICP/MS without the DRC. Figure 5-2 presents the GC-ICP/MS chromatogram obtained under these conditions for the different monitored isotopes (^{28}Si, ^{29}Si, ^{30}Si (secondary axis) and ^{53}Cr). The acetone solvent peak is detected on the four isotopes monitored due to the matrix interferences on silicon analysis in an organic matrix. The m/z 53 (^{53}Cr) allowed the monitoring of the carbon ($^{40}Ar^{13}C^+$) during the analysis. Among the 29 silicon species injected at 1 mg.kg^{-1}, 23 silicon compounds were detected in this analysis. Six volatile molecules were not detected because of the presence of the acetone peak on the m/z 28 due to the $^{12}C^{16}O^+$ interference.

To solve this main spectral interference and improve silicon compounds detection, the ICP/MS will be operated using the DRC in future experiments. In fact, the spectral interference on the m/z 28 mainly consists in the formation of $^{12}C^{16}O^+$ during gasolineanalysis when the injection of carbon in the plasma is continuous. Moreover, the presence of spikes considerably affects the detection of silicon species especially at low concentrations. This phenomenon was attributed to the use of an injector and torch in quartz and future experiments will be performed to minimize this problem.

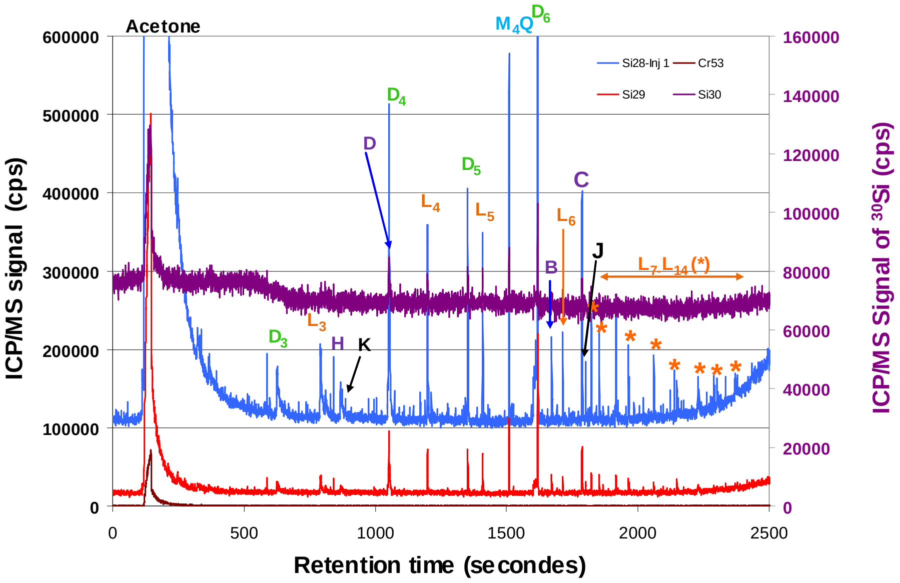
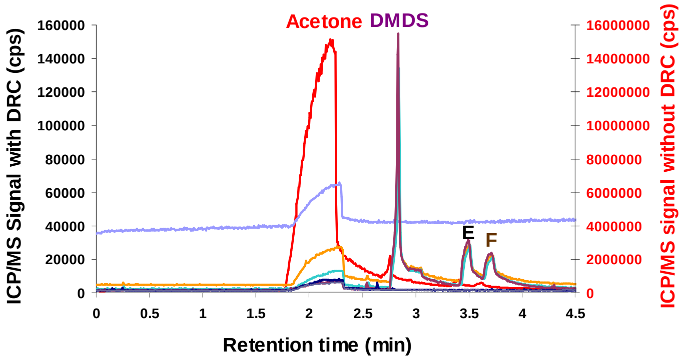
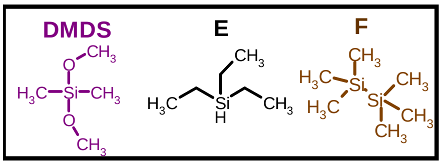


Figure 5-2. GC-ICP/MS chromatogram of the analysis of the test mixture at 1 mg.kg^{-1} without the use of the DRC and with an injection volume of 0.5 µl

5.1.4.1.2 Optimization of the DRC

According to first experiments using DRC on the ICP/MS of Perkin Elmer for total analysis of silicon in gasoline using hydrogen as the reactant gas [285], the optimization was achieved with three silicon model molecules eluted near the acetone peak. First, the number of scanned isotopes (^{28}Si, ^{29}Si, ^{30}Si, ^{53}Cr and ^{128}Xe) was reduced in order to increase the dwell time from 30 ms to 400 ms. This optimization increased the signal to noise ratio by a factor 2 for the three silicon molecules. A rapid oven ramp (30°C→80°C at 10°C.min^{-1}) was applied for the optimization in order to reduce the initial 75 minutes time of the gasoline analysis to 5 minutes. Figure 5-3 illustrates the optimization results using hydrogen as reactant gas for the DRC from 0 (without DRC) to 3 ml.min^{-1} with a variation of 0.5 ml.min^{-1}. The chromatogram obtained without the DRC is also plotted in the secondary axis of the figure to show the detection of the acetone peak.





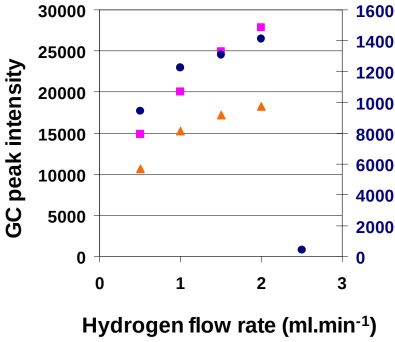


Figure 5-3. Overlay of the GC-ICP/MS chromatograms obtained during the analysis of the three silicon compounds (DMDS, E and F) obtained without the DRC and with the DRC under different hydrogen flow rates

Figure 5-4. Representation of the GC peak intensity for the three silicon compounds in function of the hydrogen flow rate injected in the DRC

With the injection of H_2 at different flow rates, the acetone peak drastically decreases without an impact on the m/z 28 signal. The noise background clearly decreases with the increase of the flow rate of hydrogen which leads to increase the signal to noise ratio (Figure 5-3). According to constant rates calculated by the NASA [288] (Table 5-3), the silicon did not react with hydrogen whereas NN^+ and CO^+ which are the main elements of interferences on m/z 28, react with hydrogen (H_2) with respectively constant rates of 2.10^{-9} and $1.5.10^{-9}$. These reactions can be explained the decrease of the spectral background noise observed using the DRC with hydrogen.

To determine the optimal value of the hydrogen flow rate, the intensity of the GC peak for the three silicon model molecules is plotted against the variation of the H_2 flow rate (Figure 5-4). Results lead to that a flow rate of 2 ml.min^{-1} gives the best signal to noise ratio for these molecules. An increase of 0.5 ml.min^{-1} on the hydrogen flow rate caused a drastic drop for the DMDS silicon compound. Compounds E and F could not be detected anymore using this flow rate. Comparising the signal to noise ratio before and after the optimization of the DRC, an increase by a factor ranging from 2 to 5 was obtained and clearly improve the detection limits.

Table 5-3. Rate constants between hydrogen and different ions of interest [288]

Gas		Ions		Reactions	Rate constant
		Si^+		No reaction	
H_2	+	NN^+	→	N_2H^+	$2x10^{-9}$
		CO^+		HCO^+	$1.5x10^{-9}$

5.1.4.2 Analytical performance of the GC-ICP/MS operated with the DRC

The use of the DRC for silicon speciation in a complex organic matrix such as gasoline is essential. This part reports the different figures of merit obtained by the GC-ICP/MS for silicon speciation respectively in acetone and in spiked gasoline to evaluate the matrix effect.

5.1.4.2.1 Detection limits and linearity

Using the GC-ICP/MS with the DRC, all silicon compounds injected were separated (Figure 5-5). The resolution of the interferences on $^{12}C^{16}O$ allowed the detection of the volatile silicon compounds (TMS, DMDS, L_2, E and F) not previously detected due to the elution of the acetone peak on the m/z 28 ($^{12}C^{16}O$ interference). In this case, the repeatability on the retention times and the detection limits were calculated.

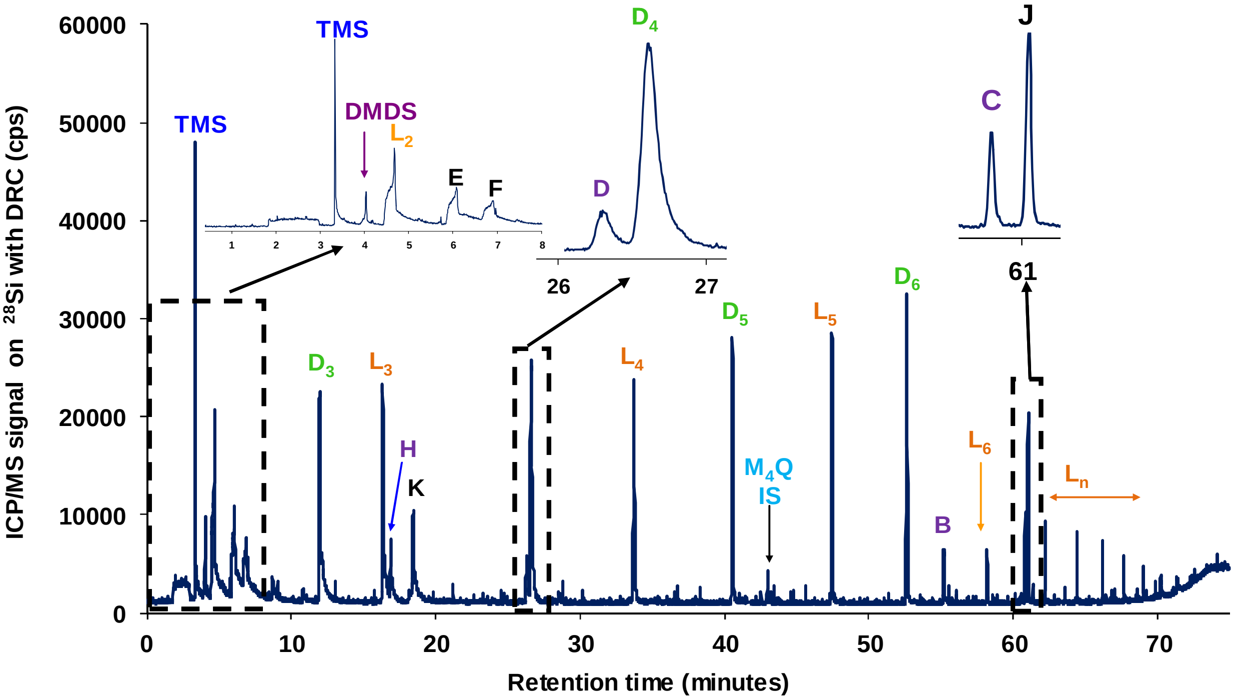


Figure 5-5. GC-ICP/MS chromatogram of the test mixture at 1mg.kg^{-1} in acetone obtained during the analysis of 1 µl in splitless mode with the same oven ramp that for a gasoline

Relative standard deviation (RSD) defined as the ratio of the standard deviation on the average is calculated on retention times for 5 replicates. Table 5-4 presents the retention times, the RSD values and detection limits obtained for silicon model molecules. The RSD value obtained for retention times were equal or lower than 0.25% and appeared as very repeatable in acetone (Table 5-4). These retention times will be used for the future calibration using the calculation of retention index to obtain the time of cuts for the identification of silicon compounds using the GC-GC/TOFMS [287].

Detection limits were calculated considering a signal to noise ratio of 3 for each silicon compounds at 1000 µg.kg^{-1} in acetone. These values were ranged from 24 to 136 µg of Si.kg^{-1} for all investigated silicon compounds (Table 5-4). Detection limits were compared to the previous values obtained using the GC-ICP/MS method without the DRC. An increase by a factor ranging from 2 to 7 on the detection limits was obtained. However, these values appeared as relatively important using ICP/MS detection. Previous detection limits obtained by GC/MS in SIM mode have showed detection limits (LOD) in a spiked gasoline ranging from 9 to 21 µg of Si.kg^{-1} for cyclic siloxanes (D_4-D_6) and between 0.35 and 2.6 µg of Si.kg^{-1} for the nine other silicon compounds [18]. The GC/MS SIM detection limits reported for D_4-D_6 were more important due to internal pollutions of the GC/MS apparatus in the split valves. The values obtained using GC-ICP/MS with the DRC (around 70 times more important than by GC/MS SIM) can be explained by the important noise background on the m/z 28. However, no contaminations by cyclic siloxanes were observed similarly to what can happen using the previous GC/MS SIM works [18].

Table 5-4. Retention times, RSD values and detection limits (LOD) of silicon model molecules

Molecules	Retention times (min)	RSD (%)	LOD (µg of Si.kg^{-1})
TMS	3.34	0.08	34
DMDS	4.04	0.19	92
L_2	4.70	0.25	46
E	6.09	0.15	90
F	6.91	0.19	136
D_3	11.97	0.06	51
L_3	16.33	0.16	67
H	16.90	0.06	100
K	18.43	0.04	84
D	26.30	0.12	122
D_4	26.61	0.05	67
L_4	33.73	0.03	66
D_5	40.56	0.02	50
M_4Q	43.02	0.03	47
L_5	47.46	0.04	47
D_6	52.63	0.02	38
B	55.19	0.04	42
C	60.83	0.26	33
J	61.04	0.19	24

Figure 5-6 presents a zoom of the previous GC-ICP/MS chromatogram between 45 and 50 minutes fitted to the elution of the L_5 silicon compound. According to the intensity calibration curve of this compound (R^2=0.997), the background equivalent concentration (BEC) was calculated as 11 µg of Si.kg^{-1}. The presence of spikes considerably affected the detection of silicon compounds and increased the background noise. The deviation of the background noise was calculated at 290 counts per second (cps) and the intensity of the background noise was stable around 1000 cps for all silicon analyses using the DRC. A value of 21 cps for 1 µg of Si.kg^{-1} was calculated taking into account the injected concentration of L_5 and the peak intensity. The deviation of the background noise was 13 times more important than the previous value and which lead to unsatisfactory detection limits to achieve a speciation of silicon at trace levels in gasoline. The offset value may be due to the use of a torch and an injector both constituted of quartz. These elements can release silicon during the analysis and considerably increase the background noise.

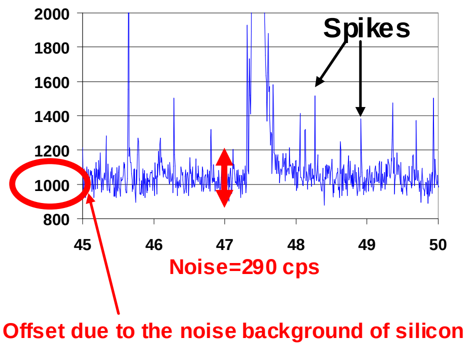


Figure 5-6. Zoom of the GC-ICP/MS chromatogram presented in Figure 24 between 45 and 50 minutes illustrating the background noise on the m/z 28 with the use of the DRC

The linearity was studied for a concentration range from 50 to 1000 µg.kg^{-1} (50, 100, 200, 500, and 1000) of silicon molecules in acetone with 5 concentrations. Figure 5-7 shows the calibration curves by chemical family (a, b, c and d) for different silicon species. The ICP/MS response is linear with correlation coefficients up to 0.99 but it is not universal for all silicon compounds. Contrary to total silicon analysis using ICP-OES [41], silicon compounds were previously vaporized and separated using GC. Therefore, they were present in the gas phase through the injector. The final temperature of the analysis was at 280°C and the temperature applied in the transfer line was set at 250°C. The transfer line was at lower temperature than the GC column and this could generate a condensation of silicon species, which would not be transferred to the ICP/MS. An increase of the temperature at 320°C (maximal temperature allowed with this equipment) could minimize this difference on the response of silicon similarly to Sanchez *et al.* works using ICP-OES [41]. In fact, the use of the torch integrated sample introduction system (TISIS) with a specific system to heat the nebulizer at 200°C (initially at ambient temperature) clearly minimizes the difference on the response of silicon compounds by ICP-OES.

For siloxanes (cyclic and linear), this non universal response is less pronounced but there is still some differences this chemical family, especially for hexamethyldisloxane (L_2), the most volatile linear siloxane. Two silanes (E and J) with boiling points respectively at 112 and 266 °C have a very different response. This phenomenon is more important for two ethoxysilane molecules. Molecules H (triethoxysilane, 141°C) and D (tetraethoxysilane, 168°C) with similar boiling points and chemical structures (Figure 5-7-c) have a difference on response factor of 3 (ratio of the relative slopes of the molecules). These results demonstrate the complexity of correlating the boiling point or the chemical form and the response of silicon compounds.

Regarding the five silicon families, a difference on the response by a factor 5.5 is observed between the silicon molecules based on slope comparison. The non universal response for silicon observed by GC-ICP/MS demonstrated the need to calculate response coefficients applied to each model silicon compound if a quantification step is necessary. Figure 5-8 presents the response coefficients calculated from the L_5 silicon compound in acetone based on the calibration curves presented in Figure 5-7. The response coefficient is calculated as the ratio between the slope of each silicon compound and the slope of M_4Q. The different families are represented with the same colour than in Figure 5-7. Response coefficients ranged from 0.32 (DMDS) and 1.73 (L_2) and confirmed the difference of the response between silicon species.

This difference on silicon compounds response was already mentioned by Grumping *et al.* [224] during the analysis of silicon compounds in biogas using low temperature (LT)-GC-ICP-OES. These authors suggested a loss of transfer or a condensation of silicon species during the transfer to the ICP. Similar trends were observed for the response of the L_2 (1.88) and or D_5 (0.89) compared to our results [224]. Several hypotheses can be suggested to explain the difference on the ICP/MS response for silicon molecules. According to Figure 5-8, all silicon compounds with a polar function (ethoxy group for DMDS, H and D; OH for TMS; or phenyl for B and J) have a low response coefficient. These molecules could be more retained in the GC column which would explain the loss of ICP/MS signal. The second hypothesis concerns the addition of argon at a high flow rate, not heated prior to the injection. This gas can cause a cold point in the transfer line and thus a loss of transfer of silicon species to the ICP/MS. Finally, the amount of carbon injected in the plasma may have also an impact but the acetone peak ($^{40}Ar^{13}C$) did not seem to tail in the different chromatograms.

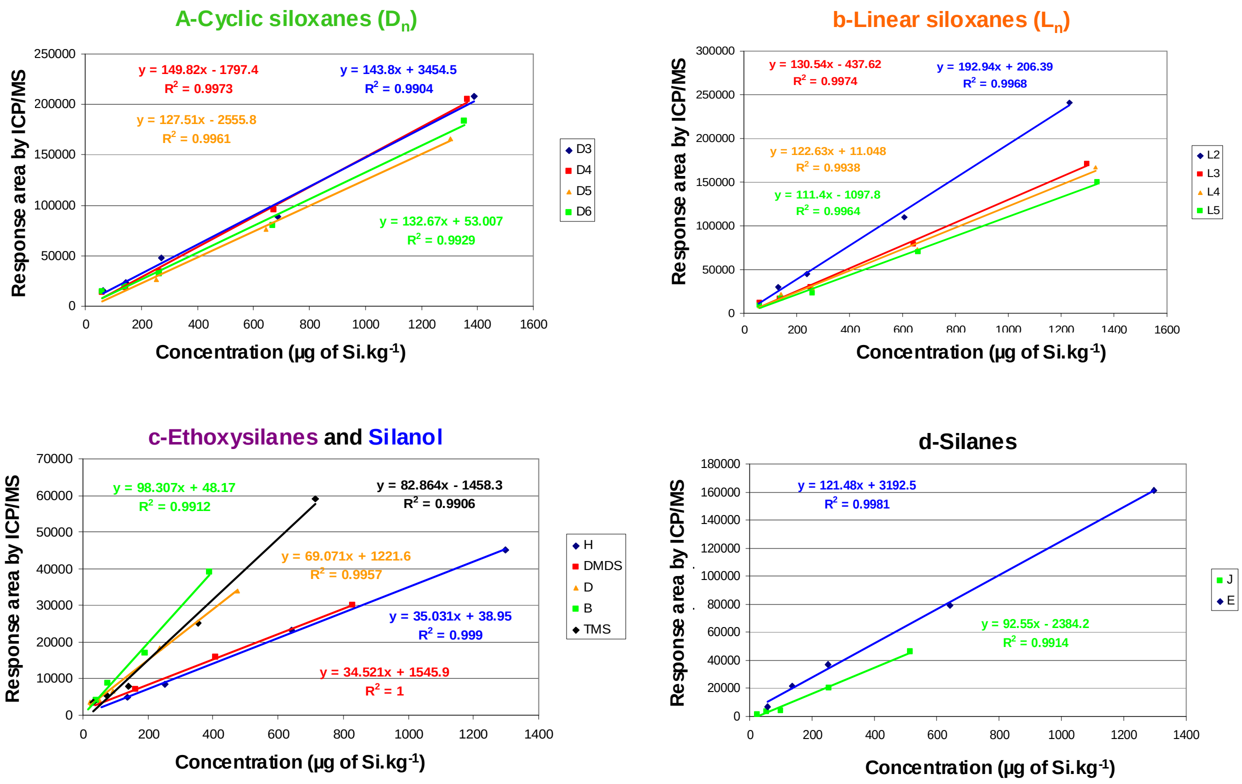


Figure 5-7. Calibration curves between 50 and 1000 µg of Si.kg^{-1} of different silicon compounds obtained by GC-ICP/MS and displayed by chemical family: a-cyclic siloxanes (D$_n$), b-Linear siloxanes (L$_n$), c-Ethoxysilanes and Silanol and d-Silanes

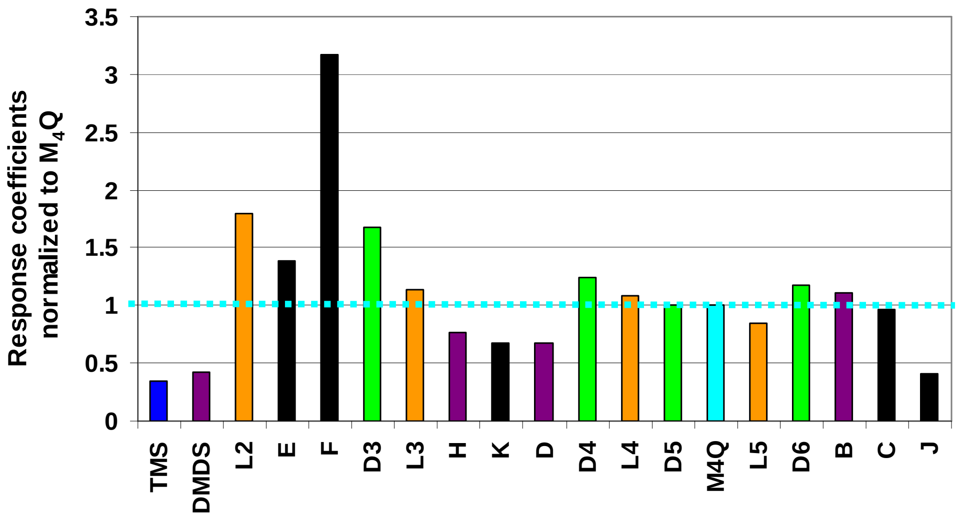


Figure 5-8. Response coefficients of silicon compounds obtained using GC-ICP/MS normalized to M$_4$Q

5.1.5 Analysis of spiked gasoline and matrix effect

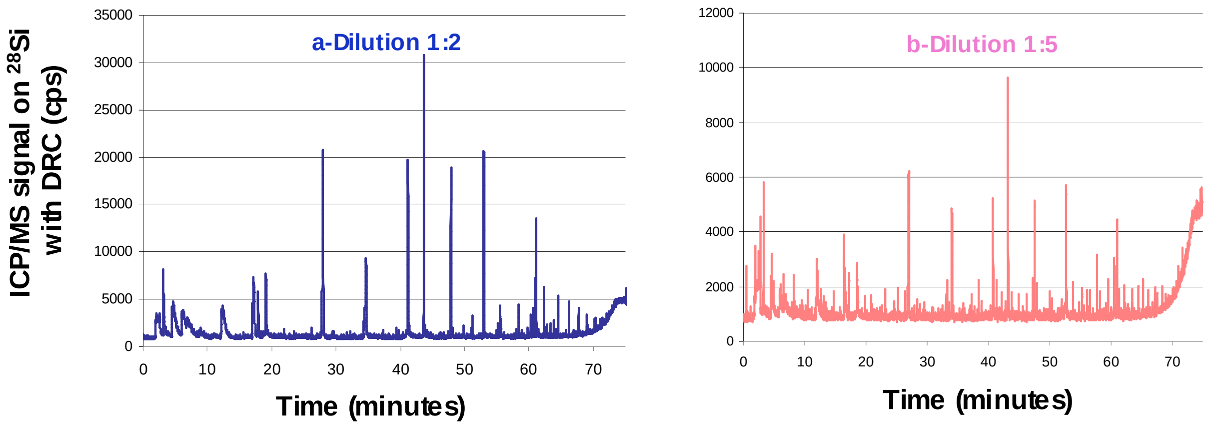
The gasoline A previously analyzed by GC/MS SIM [18] and by ESI-FT-ICR/MS [279] without traces of silicon (<5 µg of Si.kg^{-1} by ICP/MS) was used to spike silicon compounds at 1 mg.kg^{-1}. The GC-ICP/MS analysis was achieved using a volume of 1µl in splitless mode after dilution by 2 (500 µg.kg^{-1} injected), 5 (200 µg.kg^{-1} injected) and 10 (100 µg.kg^{-1} injected) in acetone.

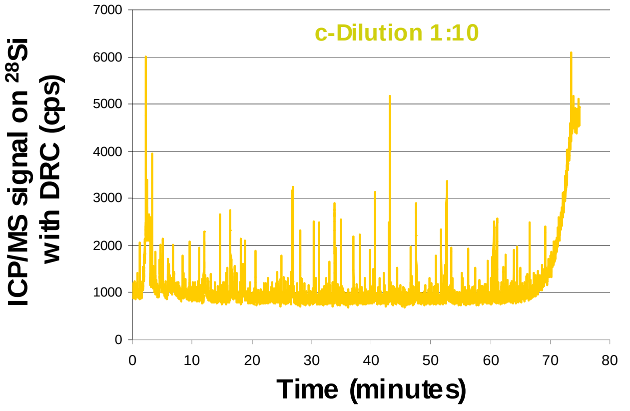
Figure 5-9 illustrates the three chromatograms and shows the separation of silicon compounds in gasoline A. The use of the DRC completely resolved the $^{12}C^{16}O^{+}$ interferences because of the continuous introduction of carbon during the GC-ICP/MS analysis. A chromatogram with the $^{40}Ar^{13}C^{+}$ (^{53}Cr) signal would allow the characterization of the hydrocarbons in the matrix. A matrix effect was clearly observed using the different dilutions in the spiked gasoline. The GC peak shape was not optimal, especially for volatile silicon compounds eluted at the beginning of the chromatogram and a shift in retention times was observed depending on the dilution ratio (Figure 5-10). These effects were clearly observed using a dilution factor of 2 in acetone. It was mainly due to the injection of 1 µl in gasoline in splitless mode to obtain a sufficient sensitivity considering both the detection limits previously obtained in acetone and the low total silicon concentration present in gasoline (Table 5-1). Due to the volume injected, the vaporization in the GC liner was not optimal. An injection in split mode was more effective for the speciation of silicon in gasoline when detection limits will be improved. When the dilution factor increased, the matrix effect and shift on retention times decreased (Figure 5-10) but detection limits increased.

As previously mentioned, the presence of spikes considerably affected the detection of silicon compounds at trace levels during the analysis (Figure 5-9). These spikes can be clearly observed using a dilution by a factor 5 and 10 but they are in fact present in all GC-ICP/MS injections. The origin of these spikes (not chromatographic peaks) may come from electronic noise because these spikes were not detected when the ^{29}Si was scanned during injection of the test mixture (Figure 5-2).

Instrumental detection limits (without taking into account the dilution factor) were calculated in spiked gasoline. Values ranged from 25 to 200 µg of Si.kg^{-1} according to the different silicon compounds. These values are as important using GC-ICP/MS, especially compared to GC/MS SIM detection limits previously obtained in spiked gasoline [18]. Future works will consist in improving the sensitivity by GC-ICP/MS. To overcome this challenge, the noise background will have to be reduced in order to decrease the injection volume (split injection) or to increase the dilution factor using a splitless dilution. The power of the plasma could also be a potential source of improvement of the sensitivity. Bouyssiere *et al.* have previously optimized the power of the plasma for the ionization of sulphur compounds in condensate gas [26]. Similar works may be considered to increase the sensitivity for silicon by increasing the ionization of silicon compounds.

After the optimization of the DRC, the analysis of model molecules, respectively in acetone and in spiked gasoline allowed to access retention times of silicon molecules in real samples. For PDMS degradation samples, a dilution by a factor 20 due to the high silicon concentration was applied to obtain a total injected concentration at 200 mg of Si.kg^{-1}. The gasoline samples coming from the refinery were analyzed after a dilution by a factor 2 in acetone in order to obtain the best sensitivity.





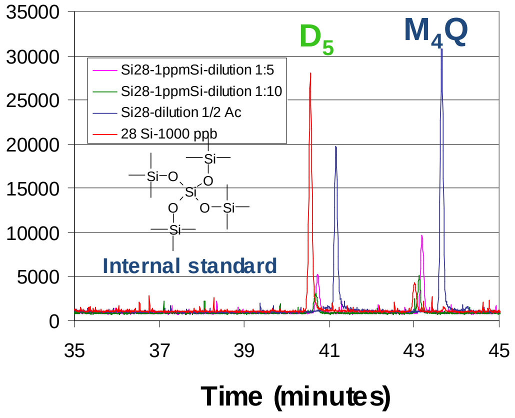


Figure 5-9. GC-ICP/MS chromatogram of the FCC gasoline spiked at 1 mg.kg^{-1} with silicon model molecules respectively diluted by a factor 2 (a), 5 (b) and 10 (c) in acetone

Figure 5-10. Zoom between 35 and 45 minutes of the chromatogram issued from the GC-ICP/MS analysis of the FCC gasoline spiked at 1 mg.kg^{-1} and diluted by a factor 2, 5 and 10 in acetone and of the test mixture at 1 mg.kg^{-1}

5.1.6 Characterization of real samples

For a complete speciation of silicon in petroleum products, an improvement of the detection limits and an universal response for silicon will be required. However, the main aim of this work is to determine the retention times of silicon compounds present in the PDMS degradation samples and in the gasoline samples in order to gain access to structural information by GC-GC/TOFMS.

5.1.6.1 Analysis of the PDMS degradation effluents

Only the samples stored in the liquid nitrogen were presented in this section. All degradation tests achieved at 500°C were analyzed using GC-ICP/MS. Figure 5-11 illustrates the GC-ICP/MS chromatogram obtained for the analysis of the degradation test B. This test was illustrated because of the greater number of silicon species detected than for the other tests. The degradation of PDMS mainly formed cyclic siloxanes (D_3-D_{16}) and confirmed the previous works achieved by GC/MS SIM [18] and by ESI-FT-ICR/MS [279] in naphtha and gasolines samples. These silicon compounds were relatively well-known as being the main PDMS thermal degradation compounds [9-11, 13] but no study had shown the potential poisoning effect of these molecules [14].

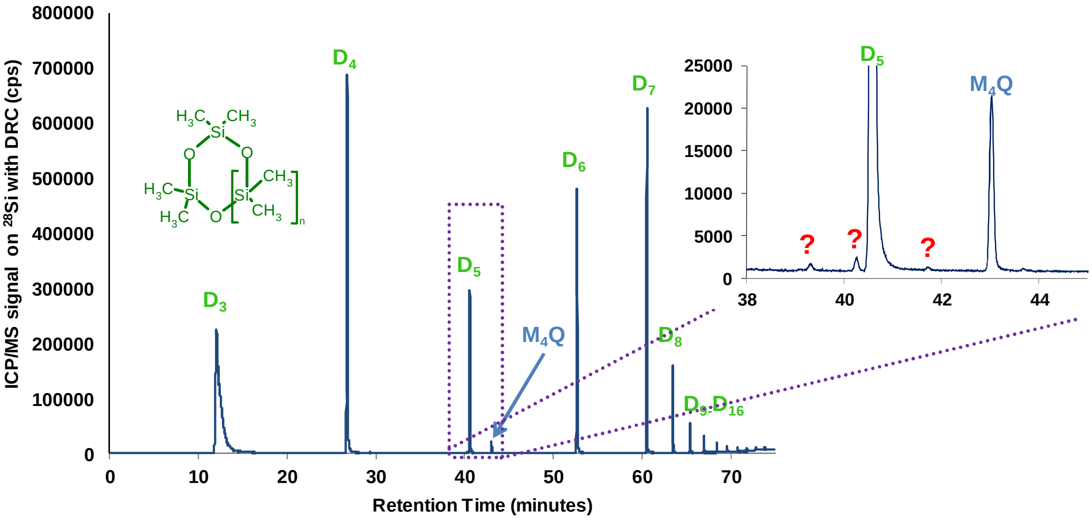


Figure 5-11. GC-ICP/MS chromatogram obtained for the degradation test B (500°C-short residence time and 50% in mass of steam)

As previously described by ESI-FT-ICR/MS [279], some other silicon compounds were produced during PDMS thermal degradation, especially in the presence of hydrocarbons and steam. A zoom of the GC-ICP/MS chromatogram presented in Figure 5-11 between 38 and 45 minutes indicates the presence of several unknown silicon compounds, eluted near the D_5 and M_4Q silicon molecules (Figure 5-11). These molecules were characterized thanks to the specific detection for silicon but were only evidenced by their retention times and the isotopic signature of the ICP/MS. The next step will consist in their characterization by GC/TOFMS and if coelutions appeared by GC-GC/TOFMS in order to obtain their mass spectrum and their chemical structure. More than 15 unknown silicon species were characterized in the different samples of PDMS degradation studies. The retention times and the retention indices of these molecules and the silicon model molecules (TMSOH, D_n) are represented in Table 5-5.

Table 5-5. Retention times of silicon compounds detected by GC-ICP/MS in all degradation tests performed at 500°C (tests B, C, D and E)

Compounds	Indices	B	C	D	E
?	0.71	n.d.	n.d.	0.77	n.d.
TMS	1.00	n.d.	n.d.	3.33	3.33
L_2	2.00	n.d.	n.d.	n.d.	n.d.
D_3	3.00	12.07	12.13	12.18	12.24
?	3.90	n.d.	23.79	23.8	n.d.
D_4	4.00	26.78	26.85	26.88	26.83
?	4.08	28.06	28.12	28.11	28.11
?	4.16	n.d.	29.00	n.d.	n.d.
?	4.19	29.36	n.d.	29.41	29.41
?	4.82	n.d.	n.d.	38.07	38.07
?	4.91	39.32	n.d.	39.36	39.36
?	4.97	40.25	n.d.	40.27	40.27
D_5	5.00	40.62	40.59	40.58	40.58
?	5.10	41.74	n.d.	41.75	41.75
M_4Q	5.20	43.03	43.06	43.03	43.03
?	5.26	n.d.	n.d.	43.71	43.71
?	5.71	49.13	n.d.	49.15	49.15
?	5.76	49.78	n.d.	n.d.	n.d.
?	5.81	50.28	n.d.	50.3	n.d.
?	5.94	51.78	n.d.	n.d.	n.d.
D_6	6.00	52.66	52.66	52.63	52.63
D_7	7.00	60.53	60.53	60.52	60.52
D_8	8.00	63.48	63.48	63.48	63.48
?	8.62	65.28	n.d.	n.d.	n.d.
D_9	9.00	65.43	65.43	65.43	65.43
D_{10}	10.00	67.00	67.00	67.00	67.00
D_{11}	11.00	68.38	68.38	68.38	68.38
D_{12}	12.00	69.6	69.6	69.6	69.6
D_{13}	13.00	70.73	70.73	70.73	70.73
D_{14}	14.00	71.8	71.8	71.8	71.8
D_{15}	15.00	72.79	72.79	72.79	72.79
D_{16}	16.00	73.82	73.82	73.82	73.82

n.d.: not detected in this sample

5.1.6.2 Analysis of naphtha and gasoline

Even if the detection limits were not completely satisfactory for the analysis of gasoline samples containing traces of total silicon, different samples were analyzed after a dilution by a factor 2 in acetone. The main aim was to determine the retention times of silicon compounds and then to identify these molecules with the GC-GC/TOFMS coupling.

Figure 5-12 presents the GC-ICP/MS chromatogram of the naphtha 2 coming from a steam cracking process. Obviously, cyclic siloxanes are observed in this sample and confirmed the results obtained by GC/MS SIM [18] and by FT-ICR/MS [279]. Using SIM mode, only known silicon compounds previously characterized by their mass spectrum could be detected because their specific ions must be chosen for the analysis. Thus, a difference between total silicon obtained by GC/MS SIM and by ICP-OES clearly indicates the presence of other completely unknown silicon compounds [18]. ESI-FT-ICR/MS proved their existance but it was impossible to determine their chemical structure.

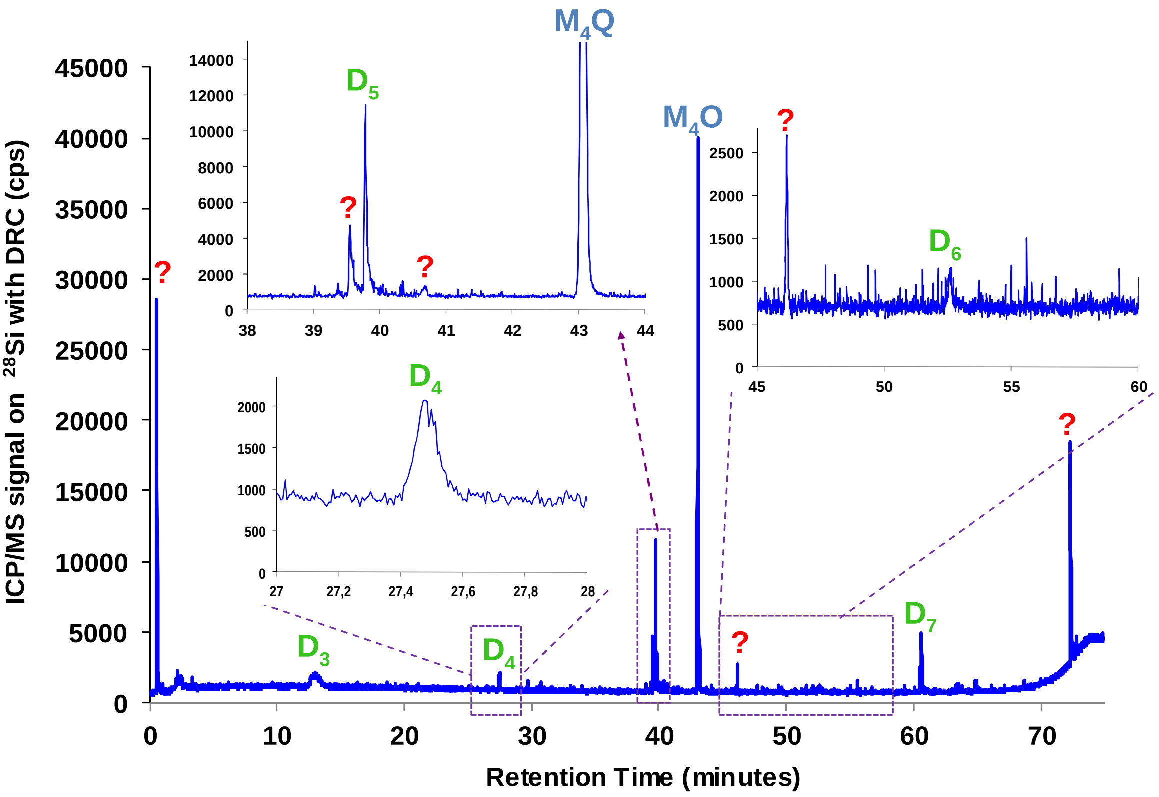


Figure 5-12. GC-ICP/MS chromatogram obtained for the analysis of the naphtha 2 with an injection volume of 1 µl in splitless mode

Similarly to the section 5.1.6.1, unknown silicon species were detected in this naphtha sample. Around the D_5 peak, a similar elution profile for unknown silicon compounds in naphtha 2 (Figure 5-12) than for the PDMS degradation test B was observed (Figure 5-11). There was a shift in retention times values between PDMS degradation samples and gasoline samples due to matrix effects. However, this will be further corrected using retention index calibration (Section 1-Annexe 6). This result confirmed the correct representativity of the production of the PDMS degradation samples under thermal cracking of hydrocarbons. Around 10 silicon species were detected in all naphtha and gasoline samples analyzed in this work. The different retention times and indices are indicated in Table 5-6 and will be of considerable interest for the future characterization using GC-GC/TOFMS giving access to their chemical structure.

Table 5-6. Retention times of silicon compounds detected by GC-ICP/MS in naphtha and gasolines samples coming from different refinery processes

Compounds	Indices	N1	N2	G3	G5	6457	6458	S7578
?	0.71	n.d.	0.57	n.d.	n.d.	n.d.	n.d.	n.d.
TMS	1.00	n.d.	3.39	n.d.	n.d.	n.d.	n.d.	n.d.
D_3	3.00	12.76	12.95	12.64	12.44	12.63	n.d.	12.59
D_4	4.00	27.29	27.48	n.d.	29.07	n.d.	27.47	26.87
?	4.97	n.d.	39.55	n.d.	39.6	n.d.	n.d.	n.d.
D_5	5.00	40.72	39.78	n.d.	40.04	n.d.	n.d.	n.d.
?	5.10	n.d.	n.d.	n.d.	41.48	n.d.	n.d.	n.d.
?	5.17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	42.20
M_4Q	5.20	43.08	43.09	43.40	43.85	43.63	43.02	43.94
?	5.34	n.d.	n.d.	n.d.	44.44	n.d.	n.d.	n.d.
?	5.46	46.2	46.18	n.d.	46.14	n.d.	46.13	n.d.
?	5.76	n.d.	n.d.	46.62	46.9	46.63	n.d.	n.d.
?	5.79	n.d.	n.d.	n.d.	47.7	n.d.	n.d.	47.71
D_6	6.00	52.64	52.64	52.80	52.80	52.76	52.46	52.68
D_7	7.00	60.53	60.64	60.57	60.57	60.55	60.47	60.64
?	7.59	n.d.	n.d.	60.67	60.73	60.69	60.64	n.d.
?	8.41	n.d.	72.32	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. : not detected in this sample

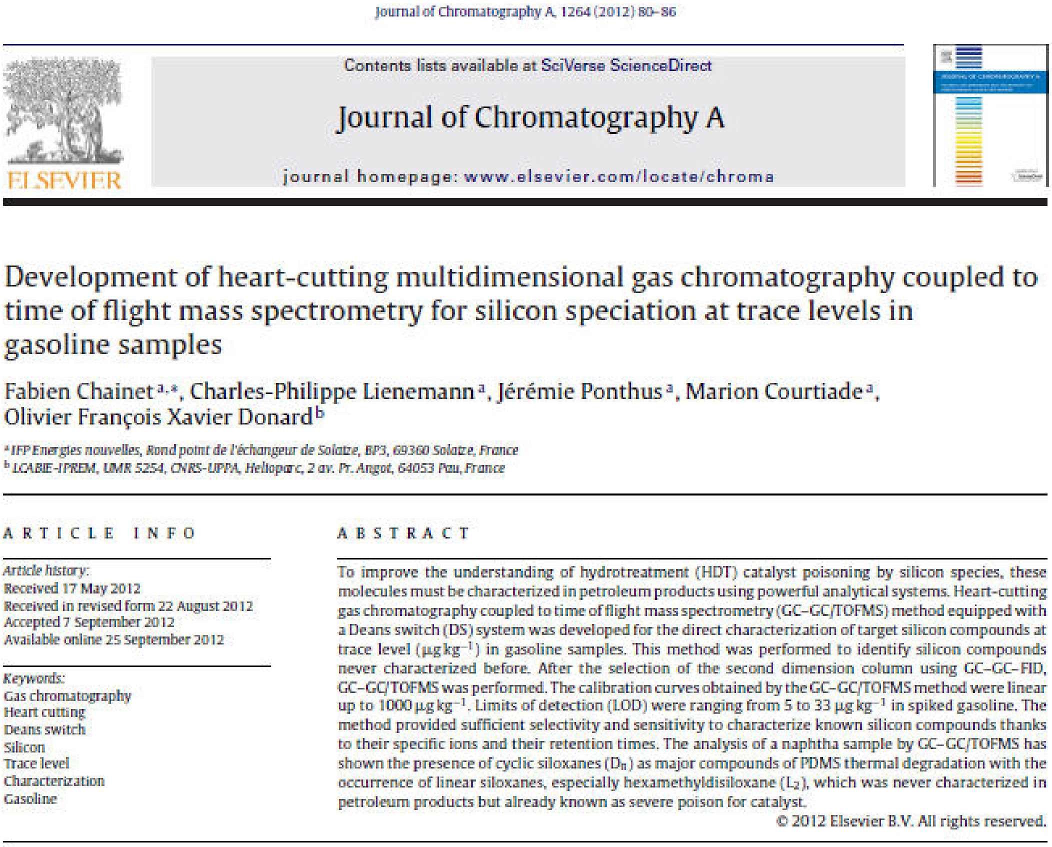
5.1.7 Conclusions

To limit the poisoning effect of hydrotreatment catalysts by silicon, all species formed by the PDMS degradation in petroleum products must be characterized by their chemical structure. Several known and commercially available silicon compounds such as cyclic siloxanes (D_n) were identified and quantified by GC/MS SIM. According to a comparison of the total silicon content obtained by GC/MS SIM and by ICP-OES measurements, other silicon molecules were present and must be identified in hydrotreatment feeds.

The aim of this work is to characterize unknown silicon species by their retention times using GC-ICP/MS thanks to the specific detection for silicon. Using the retention times obtained by GC-ICP/MS, future works by GC-GC/TOFMS will allow the characterization of silicon compounds by their chemical structure. The spectral interferences on the m/z 28 essentially concerned the formation of $^{12}C^{16}O$. This problem was successfully resolved using the DRC with the addition of hydrogen as reactant gas in acetone and especially in gasoline where the injection of carbon is continuous. After the optimization of the DRC, instrumental detection limits were calculated and were ranged from 20 to 140 µg of Si.kg^{-1} depending on the silicon model molecules. These values appeared as important using an ICP/MS detection but these LOD could be explained by the important background in silicon recovered. The torch and the injector made of quartz could be responsible of the release of silicon in the plasma. Even if the linearity was excellent, the ICP/MS response did not give an universal response for silicon and the calculation of response coefficients for the quantification of known silicon compounds is necessary.

Cyclic siloxanes (D_n) were confirmed at the major degradation products of PDMS thermal degradation but GC-ICP/MS analysis of PDMS degradation samples and real gasoline samples demonstrated the occurrence of a wide array of silicon species. Thanks to the specific detection of the ICP/MS, more than 15 new silicon species were characterized for the first time in PDMS degradation samples and more than 10 silicon molecules in gasolines samples. These compounds were present at very low concentrations compared to cyclic siloxanes and were characterized by their retention times. Future works will consist in their characterization by GC-GC/TOFMS giving access to their mass spectrum. Moreover, an optimization of the GC-ICP/MS is clearly necessary regarding the detection limits and the non universal response for silicon. To unravel this analytical challenge, several GC-ICP/MS experiments with other materials than quartz could be proposed and will be the subject of further investigations. Some other experiments will be also achieved to reduce the dependence of the chemical form with response of the ICP/MS detection. These developments will allow to propose a speciation method for silicon in the oil and gas industry using GC-ICP/MS.

5.2 Development of heart-cutting multidimensional gas chromatography coupled to time of flight mass spectrometry for silicon speciation at trace levels in gasoline samples



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Development of heart-cutting multidimensional gas chromatography coupled to time of flight mass spectrometry for silicon speciation at trace levels in gasoline samples

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ABSTRACT

To improve the understanding of hydrotreatment (HDT) catalyst poisoning by silicon species, these molecules must be characterized in petroleum products using powerful analytical systems. Heart-cutting gas chromatography coupled to time of flight mass spectrometry (GC–GC/TOFMS) method equipped with a Deans switch (DS) system was developed for the direct characterization of target silicon compounds at trace level ($\mu g\,kg^{-1}$) in gasoline samples. This method was performed to identify silicon compounds never characterized before. After the selection of the second dimension column using GC–GC–FID, GC–GC/TOFMS was performed. The calibration curves obtained by the GC–GC/TOFMS method were linear up to 1000 $\mu g\,kg^{-1}$. Limits of detection (LOD) were ranging from 5 to 33 $\mu g\,kg^{-1}$ in spiked gasoline. The method provided sufficient selectivity and sensitivity to characterize known silicon compounds thanks to their specific ions and their retention times. The analysis of a naphtha sample by GC–GC/TOFMS has shown the presence of cyclic siloxanes (D_n) as major compounds of PDMS thermal degradation with the occurrence of linear siloxanes, especially hexamethyldisiloxane (L_2), which was never characterized in petroleum products but already known as severe poison for catalyst.

5.2.1 Introduction

Silicon speciation has recently gained interest in the oil and gas industry due to the poisoning effect of silicon species on hydrotreatment (HDT) catalysts [14]. Silicon can induce catalytic deactivation and important economic losses due to untimely catalyst replacement [2]. Indeed, silicon compounds mainly originate from the thermal degradation of polydimethylsiloxanes (PDMS). PDMS is used as an antifoaming agent in different refining processes such as coking, steam cracking or distillation but also as an additive to improve the oil recovery from the reservoir [5, 14, 30]. It is now essential to identify the occurrence and formation of the different silicon species in petroleum products to improve the overall oil processing steps.

In a relatively complex matrix such as gasoline, containing more than 300 compounds [261], silicon species at trace levels can not be detected by GC/MS in full scan due to the lack of selectivity and sensitivity [18]. In previous works, cyclic siloxanes (D_n) were characterized and identified in naphtha and gasolines with some traces of dodecamethylpentasiloxane (L_5) using GC/MS but in the SIM (single ion monitoring) mode which is both selective and sensitive [18]. Cyclic siloxanes are the major compounds originating from PDMS thermal degradation [18]. Other undetected molecules using SIM mode were qualitatively characterized by their raw formula using Fourier transform ion cyclotron resonance mass spectrometry in electrospray ionization mode (ESI-FT-ICR/MS) in the same samples [279]. Most of these molecules, containing double bonds or rings, may have been generated by the reaction of PDMS degradation molecules with hydrocarbon radicals at high temperature [279]. However, the chemical structure of these molecules cannot be determined using ESI-FT-ICR/MS and further analytical developments must be achieved to identify silicon molecules. Gas chromatography coupled to inductively coupled plasma mass spectrometry (GC-ICP/MS) appears as a powerful tool for the speciation of silicon due to the sensitivity and the selectivity of the detection [14]. However, the identification is only based on the retention time of commercially available silicon compounds and on the atomic signature of the ICP/MS [14].

Using GC/MS in SIM mode for silicon speciation can overcome a limited GC separation [289]. However, unknown silicon compounds can not be detected [18]. To improve the selectivity of the GC/MS method and allow the characterization of silicon compounds by their mass spectrum, the use of a second chromatographic dimension is an excellent option. The use of a conventional GC column provides a separation power ranging from 100,000 to 130,000 efficiency (N) [289]. Using a GC-GC system, the peak capacity becomes that of the primary column (n_1), plus that of the second capillary (n_2), with the latter multiplied by the number of cuts. Thus, a gain on the resolution and on the selectivity is obtained. In similar needs, Omais *et al.* used GC-GC-FID to overcome the coelutions initially observed between oxygenated compounds and hydrocarbons in a direct coal liquefaction product by GC/TOFMS [290]. Several coelutions were successfully resolved but no identification was possible using flame ionization detector (FID). The hyphenation of a mass spectrometer to a GC-GC system appears as a powerful tool with three analytical dimensions for the characterization of a limited number of target compounds in complex matrices [289]. GC-GC/MS was performed for the identification of polar species (N, S, O compounds) in aviation fuels [291] and in gasoline [292] for the determination of oxygenated and aromatics compounds. More recently, sulphur and oxygen containing compounds were also characterized using GC-GC/MS respectively in coal derived oils [293] and in algae-derived fuel oil samples [294]. To this date, this analytical strategy has not been applied to the detection of potential poisons for hydrotreament catalyst at trace levels (µg kg^{-1}) in gasoline yet.

The aim of this work is to develop a GC-GC/TOFMS method for the characterization of silicon compounds at trace levels in light petroleum products. Before this step, the selection of the second dimension column among three column sets and the verification of the effectiveness of the Deans switch (DS) device using GC-GC-FID on model silicon molecules were performed. Prior to the analysis by GC-GC/TOFMS, specific precautions concerning the minimization of silicon pollution and sample storage were applied [14, 18]. The GC-GC/TOFMS method was developed on spiked gasoline with silicon compounds to evaluate its analytical performance. A naphtha sample was analyzed to characterize silicon compounds which were present in this petroleum cut and appear as potential poisons for hydrotreatment catalysts.

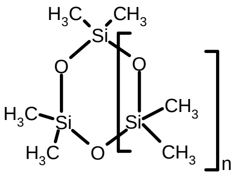
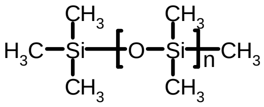
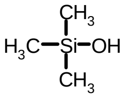
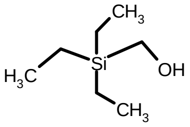
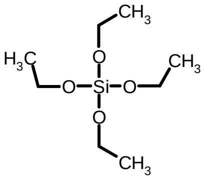
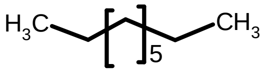
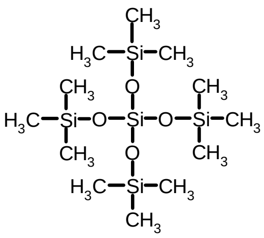
5.2.2 Experimental

5.2.2.1 Chemicals and Samples

A mixture of 12 commercially available silicon compounds based on previous studies on silicon speciation in petroleum products was used [18]. Individual standards of trimethylsilanol (TMSOH), triethylsilanol (TESOH), tetraethoxysilane (D), cyclic siloxanes (D_3-D_6), linear siloxanes L_n (L_2-L_5) and tetrakis(trimethylsilyloxy)silane (M_4Q), used as internal standard, were purchased from Sigma-Aldrich (Lyon, France). The n-nonane provided by Sigma-Aldrich (Lyon, France) was also used to select the best second dimension column. In real samples, silicon compounds present at trace levels may coelute with hydrocarbons but also with other silicon compounds. To overcome these coelutions observed on the first dimension column DB-5 MS UI, resolution on the second dimension column respectively between a selected n-paraffin (n-nonane, 151°C) and a silanol (TESOH, 158°C) and between tetraethoxysilane (D, 168°C) and octamethylcyclotetrasiloxane (D_4, 174°C) will be calculated to select the column configuration. Model compound properties are summarized in Table 5-7. Acetone of LV-GC grade, especially for trace analysis, was obtained from Biosolve Chemicals (Valkenswaard, Netherlands). The complete analytical procedure of storage to avoid contamination was previously described in Chainet *et al.* [18].

A gasoline sample, coming from a fluid catalytic cracking process with no traces of silicon (LOD<5µg.kg^{-1} of Si by ICP/MS [18]) was used to spike silicon compounds. A naphtha coming from a coking process was then analyzed by GC-GC/TOFMS. The coking process was used to crack at 500°C heavy products into lighter petroleum cuts. All samples were spiked with 200 µg.kg^{-1} of M_4Q (internal standard) in order to control the mass spectrometer variations and to achieve quantification.

Table 5-7. Model compounds contained in the test mixture

Molecules (Abbreviations)	Raw formula	BP (°C)	MM (g mol^{-1})	Chemical Structure
Silicon compounds				
Hexamethylcyclotrisiloxane (D_3)	$C_6H_{18}O_3Si_3$	134	222	
Octamethylcyclotetrasiloxane (D_4)	$C_8H_{24}O_4Si_4$	175	296	
Decamethylcyclopentasiloxane (D_5)	$C_{10}H_{30}O_5Si_5$	211	370	
Dodecamethylcyclohexasiloxane (D_6)	$C_{12}H_{36}O_6Si_6$	245	444	
Hexamethyldisiloxane (L_2)	$C_6H_{18}OSi_2$	100	162	
Octamethyltrisiloxane (L_3)	$C_8H_{24}O_2Si_3$	153	236	
Decamethyltetrasiloxane (L_4)	$C_{10}H_{30}O_3Si_4$	194	310	
Dodecamethylpentasiloxane (L_5)	$C_{12}H_{36}O_4Si_5$	210	384	
Trimethylsilanol (TMSOH)	$C_3H_{10}SiO$	98	90	
Triethylsilanol (TESOH)	$C_6H_{16}OSi$	158	132	
Tetraethoxysilane (D)	$C_8H_{20}O_4Si$	168	208	
Hydrocarbon				
n-nonane	C_9H_{20}	151	128	
Internal standard				
Tetrakis(trimethylsiloxy)silane	$C_{12}H_{36}O_4Si_5$	106	384	

5.2.2.2 GC-GC/TOFMS

The GC-GC/TOFMS experiments were carried out using an Agilent gas chromatograph 7890 (Agilent technologies, Massy, France) equipped with a Dean switch device (model G2855B, Agilent Technologies, Burwood, Australia) [295] and two flame ionization detectors (FID) coupled to a time of flight mass spectrometer (TOFMS) (AccuTOF GC, JEOL, Tokyo, Japan). Figure 5-13 presents the scheme of the apparatus. Under normal analytical conditions, the system valve of the Deans switch (DS) is off and all the analytes eluted on the first column were detected using the front FID (Figure 5-13). To transfer the fraction from the first dimension to the second dimension coupled to the TOFMS detection, the DS valve must be on. This action of transfer was called "to cut" in the paper. Then, a second column with a different selectivity allows the separation of the two co-eluted peaks which can be then identified thanks to their mass spectrum (Figure 5-13).

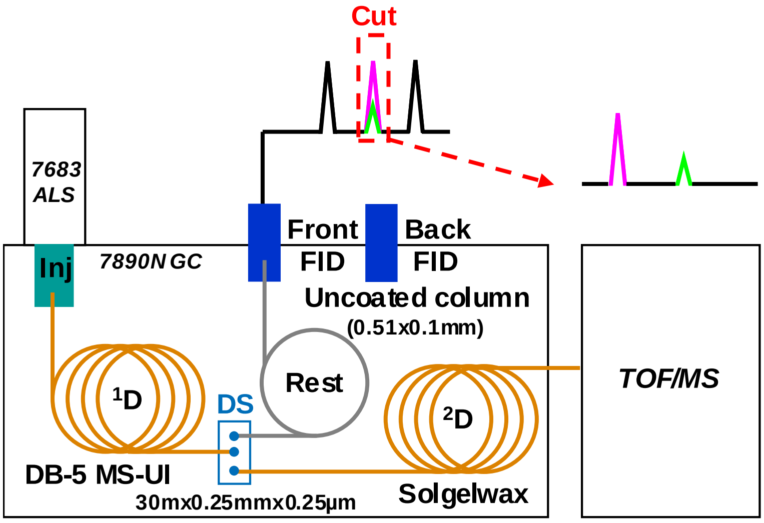


Figure 5-13. Schematic diagram of the GC-GC/TOFMS instrument. Inj, Inlet; ^{1}D, first column; DS, Deans switch; Rest, uncoated column; front FID and back FID, flame ionization detectors; ^{2}D, second column; TOFMS, time of flight mass spectrometer (Adapted from [296])

A DB-5 MS UI (ultra-inert) column (5%-phenyl and 95%-dimethylpolysiloxane, J&W Scientific, Folsom, CA, USA) was used on the first dimension (30m x 0.25mm i.d., 0.25µm film thickness). This column has been previously identified and used to allow the separation of silicon compounds from hydrocarbons in a gasoline by GC/MS SIM [18] and by GC-ICP/MS [297]. Thanks to the specific detection of the GC-ICP/MS, unknown silicon species were detected by their retention times but the chemical structure can not be determined without silicon compounds commercially available. The retention times of unknown silicon compounds were obtained and the fraction containing the silicon compound eluted in the first column (DB-5 MS UI) can be then transferred to the second dimension coupled to the

TOFMS for the characterization of the molecule. This column was retained as the first dimension for the three sets. To calibrate the retention times obtained by GC-FID, GC/TOFMS and also GC-ICP/MS, retention indices were calculated to obtain a same value of retention whatever the detector used.

The initial uncoated restrictor used for the FID detection (0.77m x 0.1mm i.d.) was modified using the TOFMS (0.51m × 0.10mm i.d.) and was placed between the first column and the front FID detector to compensate for the pressure drops in the second dimension. For the second dimension of separation, three different columns with the same geometry of the first dimension (30m x 0.25 mm i.d., 0.25µm film thickness) were investigated: Rtx-200 MS (trifluoropropylmethylpolysiloxane, Restek, Lisses, France), DB-1701 (14%-cyanopropylphenyl and 86%-dimethylpolysiloxane, J&W Scientific, Folsom, CA, USA) and Solgelwax (polyethylene glycol, SGE, Keynes, United Kingdom).

A volume of 0.5µl with a split ratio 1:50 was injected at a temperature of 200°C through a Merlin microseal septum (Merlin Instrument Company, Half Moon Bay, CA, United States) free of silicon to avoid contamination by cyclic siloxanes (D_n) observed with a classical septum [18]. The carrier gas was helium (99.99% Air liquide, France). The primary, secondary and restrictor flows were respectively equal to 1.0, 1.4 and 1.4 ml. min^{-1}. The ionization source was heated at 200 °C and operated using electron ionization (EI) at 70 eV. The MS acquisition was performed in full scan mode for a mass range from m/z 10 to m/z 500. The mass spectra were compared to the combined Wiley Registry 9th Edition (John Wiley & Sons, Inc., New York, USA, 2010) / NIST 2011 Mass Spectral Library (National Institute of Standards and Technology, Gaithersburg, MD, USA version 2011). To improve the selectivity of the TOFMS, extracted ion chromatogram (EIC) was also obtained from the total ion current (TIC) chromatogram. The raw data were respectively acquired using the Chemstation software (Agilent technologies, Massy, France) for front FID chromatogram on the first dimension and with the Mass Center software (JEOL, Tokyo, Japan) for the TOFMS chromatogram on the second dimension.

In this paper, the GC-GC/TOFMS was developed in spiked gasoline and applied to a naphtha sample. Commercially available silicon compounds were characterized by their retention times and specific ions. The chemical structure of unknown compounds can not be determined due to the complexity of the matrix and trace level silicon concentration. The method will be applied to PDMS degradation samples with higher silicon content and a lower matrix complexity. The final aim will be the characterization of molecules by their complete mass spectrum which can lead to their structural identification. This work will be the subject of a further paper.

5.2.3 Results and Discussion

The first experiments were performed using the GC-GC-FID system for the selection of the second dimension column using three column sets and the verification of the Deans switch device reliability. Then, the development of the GC-GC/TOFMS was carried out in order to characterize trace level silicon compounds in gasoline samples, potentially responsible of catalyst poisoning.

5.2.3.1 Colum selection experiment

To evaluate the performance of the three column sets, resolution on the second dimension column between n-nonane and TESOH was calculated as well as the one between the two silicon compounds. The use of a second dimension column with a different selectivity was investigated to improve the separation of these compounds, initially coeluted on the first dimension (Figure 5-14). Resolution results are indicated in Table 5-8. They show the correct separation of n-nonane from TESOH for the three cases with a better resolution obtained for set Z (DB-5 MS UI x Solgelwax). The separation on the DB-5 MS UI column (5%-phenyl and 95%-dimethylpolysiloxane) is mainly governed by volatility whereas DB-1701 and solgelwax columns separate analytes by polarity. As recently reported by Omais *et al.* [298], it was necessary to consider the specific analyte-stationary phase interactions. In our case, TESOH has greater affinity with the second dimension stationary phase the than the n-nonane due to the phenyl groups of the DB-1701 stationary phase and the lone pairs of oxygen present in the solgelwax stationary phase. The selectivity of the Rtx-200 MS (trifluoropropylmethylpolysiloxane) seems to provide a separation by electronic interactions but is not sufficient for these two compounds.

Table 5-8. Calculated Resolution (R) on the second dimension between n-nonane (nC_9) and TESOH and between D and D_4 silicon compounds using the three sets of columns (X, Y and Z). Oven temperature program: 30°C (7min) to 120°C at 5°C/min and then to 280°C at 10°C/min (2min)

Sets	1st Col.	2nde Col.	R (nC_9 vs. TESOH)	R (D vs. D_4)
X	DB-5 MS UI	Rtx-200 MS	45.9	1.5
Y		DB1701	102.9	6.9
Z		Solgelwax	126.2	11.6

Concerning the separation of the two silicon compounds D and D_4, two column sets are adapted. Figure 5-14 (a) illustrates the front FID chromatogram obtained for their separation on the first DB-5 MS UI column with no cut transferred to the second dimension. In order to obtain a correct chromatographic separation, a gain of resolution was obtained by transferring the fraction between 18.4 and 18.7 minutes containing the two co eluted compounds, into the second column. Using set X (DB-5 MS UI x Rtx-200 MS), resolution was 1.5. This value was similar than when using one dimension of separation on the DB-5 MS UI (Table 5-8).

Figure 5-14 (b) illustrates the front FID chromatogram obtained after the cut on the first dimension to demonstrate that both compounds D and D_4 were correctly transferred to the second dimension. Figure 5-14 (c) shows the back FID chromatogram obtained for the separation on the second solgelwax column used in set Z. A reversal of the elution order for D and D_4 can be noticed on this chromatogram. This result was confirmed by each analytical standard analysis. Using the solgelwax column on the second dimension, D and D_4 which have close volatility are now separated by polarity. According to resolution results obtained for three sets, set Z provided the best separation between D and D_4 silicon compounds with an improvement of the resolution on the second dimension by a factor 7.5. This result confirmed the first selection for the separation of n-nonane from TESOH (Table 5-8). Set Z was selected for further GC-GC/TOFMS experiments.

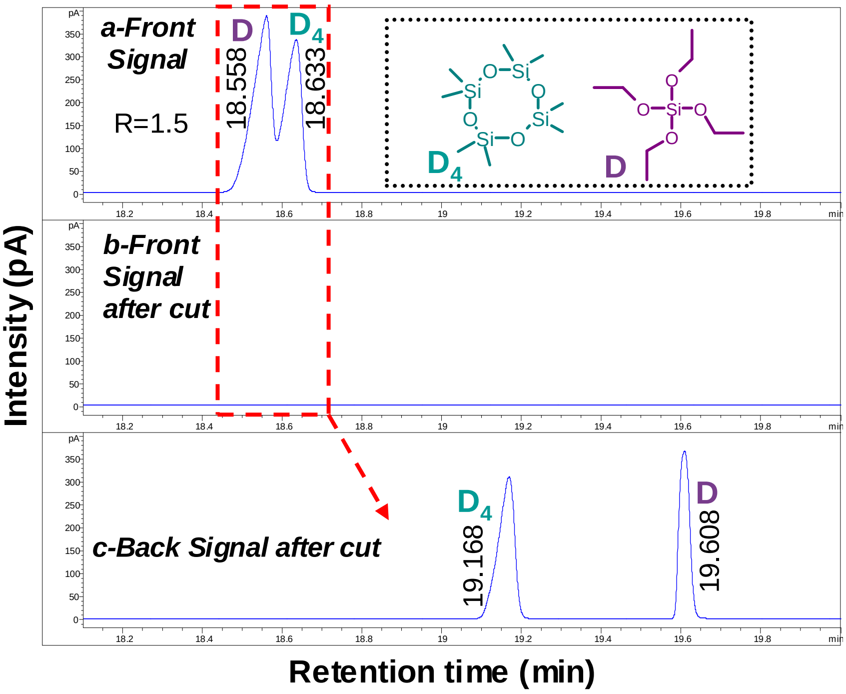


Figure 5-14. Zoom between 18 and 20 minutes of the GC-GC-front FID chromatograms observed for the separation between D and D_4 silicon standard molecules in the first dimension without cut (a-front FID chromatogram), in the first dimension with cut (b-front FID chromatogram) and in the second dimension after a cut (c-back FID chromatogram) using set Z (DB-5MS UI x solgelwax, 30mx0.25mm i.d.x0.25µm film thickness). Oven temperature program: 30°C (7min) to 120°C at 5°C.min^{-1} and then to 280°C at 10°C.min^{-1} (2min)

5.2.3.2 Deans switch device validation

The Agilent Deans switch system is an effective and robust system and many applications were reported in the literature [289, 295, 299]. However, prior GC-GC/TOFMS method with the selected set Z, it was crucial to ensure that the fraction eluting from the first dimension was completely transferred to the second dimension [289]. A mixture of linear siloxanes (L_2-L_5) which are easily separated on the first column was injected by GC-GC-FID using set Z to demonstrate the efficiency of the Deans switch. The difference between the measured peak areas on the first (1st) and on the second dimension (2nd) by GC-GC-FID was calculated. These results confirm that the difference between the first peak area and the second peak area for linear compounds is below 0.4 %. This value is in accordance with Seeley *et al.* [300] works when using the Deans switch device for comprehensive GC analysis in gasoline and demonstrates that the system is reliable with no leaks taking place during transfer.

5.2.3.3 Analytical performance of the GC-GC/TOFMS method

Now that the column combination was selected, the GC-GC/TOFMS method can be applied to the detection of silicon compounds in gasoline (Figure 5-14). First, the test mixture was injected by GC-GC/TOFMS without any cut to obtain the retention times on the first dimension because the retention times were a little bit different than using GC-GC-FID because of the vacuum (Table 5-9). One cut was defined for each silicon compound to allow the detection of these targeted compounds at trace levels in gasoline samples. All silicon compound retention times on the second dimension were obtained after applying the GC-GC method to the ten previously defined cuts. It was applied to the test mixture both in acetone and in spiked gasoline (Table 5-9). Thanks to their mass spectrum, all silicon compounds were characterized by their second retention time and their specific ions.

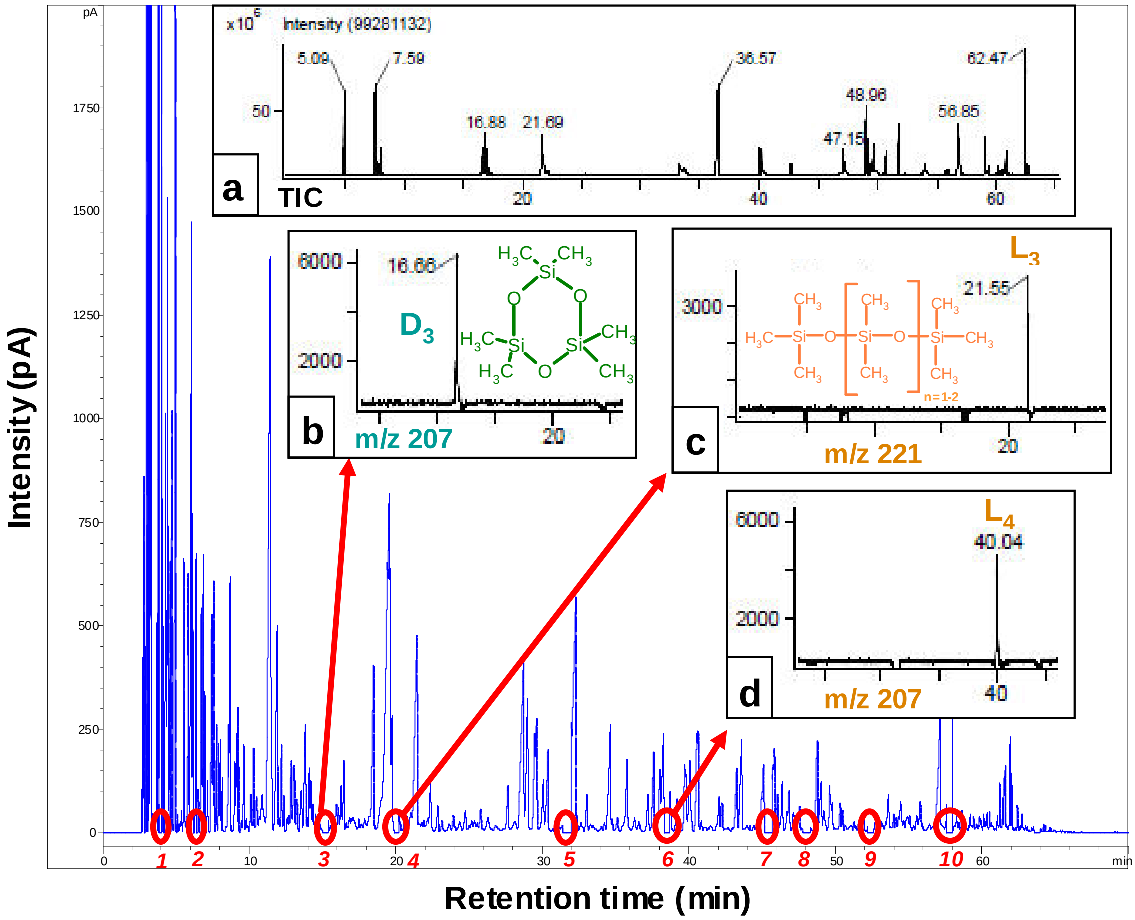


Figure 5-15. GC-GC-front FID chromatogram and GC-GC/TOFMS chromatograms (a, b, c, d) obtained for the analysis of the gasoline spiked with silicon compounds at 1000 µg.kg^{-1}. a-GC-GC/TOFMS TIC chromatogram of all cuts; b-GC-GC/TOFMS EIC m/z 207 obtained for D_3; c-GC-GC/TOFMS EIC m/z 221 obtained for L_3; d-GC-GC/TOFMS EIC m/z 207 obtained for L_4. Oven temperature program: 30°C (7min) to 50°C at 2°C.min^{-1}, then to 60°C at 1°C.min^{-1}, then to 120°C at 2°C.min^{-1} and then to 280°C (2min) at 10°C.min^{-1}

Due to the complexity of the gasoline matrix in general with more than 300 compounds eluted, silicon compounds present at trace levels cannot be detected using only one dimension of separation coupled to MS performed in full scan mode [18]. Figure 5-15 presents the GC-GC-front FID chromatogram obtained on the first dimension for the analysis of the gasoline spiked with ten silicon compounds at 1000 µg.kg^{-1}. Each fraction eluted on the first dimension and containing the silicon compounds with highly concentrated hydrocarbons was transferred to the second dimension coupled to the TOFMS. Figure 5-15 (a) presents the TIC GC-GC/TOFMS chromatogram obtained for the 10 cuts. Despite of the short time of each fraction transferred (Table 5-9), silicon compounds cannot be detected among the hydrocarbons. These targeted compounds were present at trace level concentrations and were unseparated from hydrocarbons after the two dimensions of separation. Thus, the identification of the silicon compound was not achievable. To overcome these coelutions, the three most abundant ions of each compound were extracted from the TIC chromatogram to characterize silicon compounds at trace levels in gasoline samples [18]. Figure 5-15 (b, c and d) illustrates the EIC of three silicon compounds (D_3, L_3 and L_4) by GC-GC/TOFMS among the 10 silicon compounds chosen in this work.

Table 5-9. Retention times (1st and 2nd), heart-cut times, calibration results of the GC-GC/TOFMS for silicon compounds spiked in gasoline and results of the naphtha analysis

M	1st t_R	Cuts	2nd t_R	LOD	Equation		Naphtha
	(min)			µg.kg^{-1}	y=ax+b	R²	Concentration (µg.kg^{-1})
TMSOH	3.90	(1) 3.70-4.00	9.16	33	7.37x-663	0.999	n.d.
L_2	6.43	(2) 6.35-6.51	7.65	7	36.04x-1722	0.998	60±3
D_3	15.23	(3) 15.02-15.38	16.68	17	32.05x-1596	0.999	973±27
L_3	20.06	(4) 19.90-20.20	21.45	7	17.52x+557	0.998	n.d.
D_4	31.78	(5) 31.40-32.00	33.28	5	29.91x+362	0.997	373±14
L_4	38.54	(6) 38.35-38.70	40.03	16	18.91x+174	0.999	105±6
D_5	45.50	(7) 45.20-45.70	46.87	6	6.41x-40	0.999	671±15
M_4Q	48.09	(8) 47.80-48.30	49.36	21	n.c.	n.c.	int. std.
L_5	52.42	(9) 52.20-52.60	53.86	22	4.54x+190	0.996	n.d.
D_6	57.82	(10) 57.60-58.00	59.00	12	3.81x-116	0.999	459±12

n.d. not detected; n.q. not quantified; n.c. not calculated; int. std. internal standard

Limits of detection and quantification were calculated respectively considering a signal to noise of 3 and 10 in gasoline spiked with 100 µg.kg^{-1} of silicon molecules. Limits of detection are ranging from 5 to 33 µg.kg^{-1} depending on their TOFMS response (Table 5-9). The calibration curves for all compounds were linear from 50 to 1000 µg.kg^{-1} with correlation coefficients above 0.996. The TOFMS response was very stable (less than 5% variation on the peak area of M_4Q used as internal standard). Due to the difference of response for silicon compounds, the quantification approach was based on the calculation of response factors using calibration curves and normalization with D_3.

LOD values for linear siloxanes and D_3 are consistent with previous works achieved in gasoline by GC/MS in SIM mode [18]. For cyclic siloxanes (D_4-D_6), the minimization of the contaminations allowed an improvement of LOD by a factor ranging from 3 to 10. This was obtained since no silicon septum was never used before and since the GC was continuously operated with the Merlin system. Using previous GC/MS SIM experiments [18], volatile silicon compounds (TMSOH, L_2) could not be detected. The same fragmentation ions between highly concentrated hydrocarbons and silicon compounds eluted at the beginning of the chromatogram were observed. This problem was overcome by GC-GC/TOFMS and further discussed in the next section.

This GC-GC/TOFMS method allowed the characterization of silicon species at trace level concentrations in gasoline samples. Based on the retention times determined by GC-ICP/MS, the use of the GC-GC/TOFMS will be crucial to characterize other silicon compounds

5.2.3.4 Analysis of a cokefaction naphtha sample

The method was applied to a naphtha sample originating from a coking process (Table 5-9) by GC-GC/TOFMS to characterize silicon compounds, potentially poisons for HDT catalysts. The different silicon species recovered in this sample are presented in Table 5-9. Among the ten model silicon compounds, six silicon species were characterized in this naphtha. The quantitative results are obtained for 3 replicates.

Cyclic siloxanes (D_3-D_6) were confirmed as the major degradation products in the naphtha cut. D_3 was the most abundant because it was the most thermodynamically stable at the temperature of the process [301]. Concentrations ranging from 973 to 373 µg.kg^{-1} were obtained for these silicon species. These compounds were previously identified and quantified in the same concentration range by GC/MS in SIM mode in naphtha and gasoline samples coming from a steam cracking process [18]. These molecules were produced through a depolymerization mechanism from the initial PDMS added as antifoaming before the coking process. This mechanism was previously demonstrated in the literature [10, 11, 13]. The occurrence of cyclic siloxanes was followed by the formation of linear siloxanes (L_n) at lower concentrations. However, volatile compounds such as TMSOH or L_2, potentially formed during PDMS degradation, were never characterized in petroleum products

Linear siloxanes such as L_2 and L_4 were detected in this sample at lower concentrations than the cyclic siloxanes (Table 5-9). L_4 and L_2 were respectively quantified at 105 and 60 µg.kg^{-1} in this naphtha. These results clearly confirmed that the formation of cyclic and linear siloxanes originated from PDMS thermal degradation

These silicon compounds were potentially responsible of the catalyst poisoning. Even if cyclic siloxanes (D_n) were the major PDMS degradation products, no study was reported yet on their poisoning effects. On the contrary, L_2 was previously characterized as severe poison for Pd and Pt catalysts used for the oxidation of volatile organic compounds (VOC) in a biogas plant [65, 66]. This molecule was highlighted in this sample and can come from the thermal degradation of PDMS by a depolymerization mechanism with the high production of cyclic siloxanes (D_n) [10]. Moreover, L_2 can also be formed by the self-condensation of trimethylsilanol (TMSOH) because of its high reactivity. This molecule may be initially present in the refining process and converted in L_2 between the sampling step and the analysis in the lab [302]. The evolution of silicon species was highly suspected in petroleum products and should be further investigated.

5.2.4 Conclusions

The speciation of silicon was necessary to progress on the understanding of hydrotreatment catalyst poisoning. In this paper, a novel GC-GC/TOFMS method for the characterization of silicon compounds at trace levels in light petroleum products was developed and applied to a naphtha sample. After the second column selection experiment and the verification of Deans switch reliability using GC-GC-FID, spiked gasoline was analyzed by GC-GC/TOFMS to evaluate the analytical performance. Limits of detection for all silicon compounds ranging from 5 to 33 µg.kg^{-1} were obtained and the calibration curves were linear up to 1000 µg.kg^{-1}. The GC-GC/TOFMS method provided sufficient sensitivity and selectivity for silicon compounds and allowed their characterization thanks their specific ions. Cyclic siloxanes (D_n) were characterized as the major silicon compounds in the naphtha boiling point range. Moreover, volatile silicon compounds could be also detected using this method. Hexamethyldisiloxane (L_2) was detected in this naphtha and was previously characterized as severe catalyst poison. Such a characterization of silicon species acting as a severe poison was never highlighted in petroleum products. The determination of the chemical structure of silicon compounds was crucial to improve the life cycle of catalysts and the global efficiency of the refining processes.

However, further studies focusing on the possible evolution of silicon species during storage must be achieved to characterize the molecules which are really present during the poisoning step of the HDT catalysts. The production of fresh and representative samples of PDMS degradation under refining conditions with higher concentration of silicon and a less complex matrix should be done and analyzed using a multi-technical approach. Based on their retention times determined by GC-ICP/MS, the chemical structure of unknown silicon compounds can be determined using the GC-GC/TOFMS method developed in this work

Conclusion générale de la partie B

Cette partie avait pour but de présenter les différentes méthodes analytiques développées pour la spéciation du silicium dans les produits pétroliers et en particulier dans les coupes naphtas et essences dans lesquelles le silicium pose les problèmes d'empoisonnement les plus conséquents.

La GC/MS SIM (Chapitre 3) a permis de détecter et de quantifier les composés silicés connus dans une essence à l'état de traces ($1<\mathrm{LOD}(\mu g.kg^{-1})<50$). Cette étude constitue le premier travail reporté dans la littérature concernant la spéciation du silicium effectuée dans des essences et des naphtas. Les résultats obtenus montrent que les siloxanes cycliques (D_n) sont les composés majoritairement présents dans les produits pétroliers et proviennent directement de la dégradation du PDMS. De plus, des traces de siloxane linéaire (L_5) et de tétraéthoxysilane ont également été retrouvées. Cependant, la comparaison entre la concentration totale en silicium obtenue par GC/MS SIM et par ICP-OES montre que 50% des espèces silicées sont quantifiées. En effet, la sélectivité du mode SIM nécessite de connaître les ions fragments des molécules (précédemment obtenus par leur spectre de masse) et ne permet donc pas la détection des composés inconnus.

Pour parvenir à la caractérisation de ces derniers, la méthode ESI-FT-ICR/MS associée à la construction de diagrammes de Kendrick (Chapitre 4) s'est avérée très performante pour la recherche des composés silicés inconnus appartenant à la même famille que les composés silicés modèles. En effet, les espèces silicées retrouvées diffèrent des composés modèles par leur nombre d'insaturations (DBE) et par leur nombre de carbone. En plus de la confirmation des siloxanes cycliques (D_3-D_6), plus de 50 nouvelles espèces silicées (C_2-C_{18}) appartenant aux familles O_2Si, O_3Si et O_4Si ont été caractérisées. Leur nombre d'insaturation (DBE) est compris entre zéro et huit. Cependant, l'accès à leur structure chimique est rendu difficile par le nombre conséquent d'isomères pour chaque formule brute obtenue.

Afin de connaître la structure chimique des espèces, une approche inédite entre la GC-ICP/MS (Section 5.1) et la GC-GC/TOFMS (Section 5.2) a été présentée dans le Chapitre 5. Le développement de la GC-ICP/MS a permis la mise en évidence de composés silicés totalement inconnus par leur temps de rétention, notamment grâce à la résolution des interférences sur la masse m/z 28 du silicium ($^{12}C^{16}O^+$ et $^{14}N^{14}N^+$) en utilisant une cellule de collision réaction avec de l'hydrogène comme gaz réactif. En effet, malgré des limites de détection élevées ($20<\mathrm{LOD}(\mu g$ de $Si.kg^{-1}<140)$ dans l'acétone et une réponse non universelle pour le silicium, une quinzaine et une dizaine de composés ont été détectées pour la première fois, respectivement dans les échantillons de dégradation du PDMS produits et dans des essences issues de différents procédés de raffinage. Il apparaît évident que pour disposer d'une méthode de spéciation du silicium dans les produits réels par GC-ICP/MS, des améliorations au niveau des LOD et de la quantification sont nécessaires. Néanmoins, le principal objectif a été atteint car il consistait à accéder aux temps de rétention des composés inconnus pour ensuite les identifier par GC-GC/TOFMS. Ce dernier développement a montré tout son potentiel pour retrouver les composés silicés à l'état de traces suite à leur détection par GC-ICP/MS. En effet, des LOD comprises entre 5 et 33 µg.kg^{-1} pour les composés modèles dans une essence dopée ont été obtenues. L'application de cette méthode à un naphta de cokéfaction a confirmé la présence de siloxanes cycliques (D_n) comme composés majoritaires de dégradation du PDMS et également l'identification de siloxanes linéaires tels que le L_2 et le L_4. Ce travail consistait à développer la méthode GC-GC/TOFMS dans un premier temps. Grâce aux temps de rétention des espèces silicées obtenus par GC-ICP/MS (Section 5.1) et GC/MS, son application à des échantillons de dégradation du PDMS sera présentée et discutée dans la section 7.2 de la Partie C.

A la vue de ces résultats, chaque technique permet d'apporter une information cruciale pour parvenir à avancer sur la spéciation du silicium. Le Tableau 5-1 résume les apports et limitations de chaque technique utilisée pour la spéciation du silicium dans les produits pétroliers. Dans cette optique, une combinaison des différentes techniques analytiques semble être une solution adaptée afin de déterminer la structure chimique des composés silicés, potentiellement responsables de l'empoisonnement observé.

Tableau 5-1. Apports et limitations des techniques utilisées pour la spéciation du silicium

Techniques	Apports	Limitations
GC/MS SIM	-Détection des composés silicés connus -1<LOD<50 µg.kg^{-1} (ppb) -Quantification pour les étalons disponibles commercialement	-Détection dépendante de la matrice -Composés inconnus non détectables
FT-ICR/MS	-Caractérisation des composés par leur formule brute et nombre d'insaturations -Méthode très sensible (80 ng.kg^{-1}<LOD<5 µg.kg^{-1}	-Quantification des composés inconnus impossible à effectuer -Pas d'accès à la structure chimique (nombreux isomères)
GC-ICP/MS	-Détection spécifique de tous les composés silicés par leur temps de rétention -Quantification pour les étalons disponibles commercialement	-Pas d'accès à la structure chimique des espèces inconnues -Sensibilité non optimale (50<LOD<200 µg.kg^{-1} de Si) -Réponse du silicium non universelle
GC-GC/TOFMS	-Accès au spectre de masse de la molécule silicée détectée par GC-ICP/MS -5<LOD<50 µg.kg^{-1} -Quantification pour les étalons disponibles commercialement	-Nécessité de connaître le temps de rétention des silicés (complément GC-ICP/MS) -Nombre limité de composés recherchés

Au sein de cette partie, les méthodes développées ont été validées sur des échantillons prélevés au sein de différents procédés de raffinage et stockés en chambre froide (-10°C) ou au réfrigérateur (4°C) puis analysés quelque mois plus tard. Actuellement, aucune précaution particulière n'est généralement prise entre le prélèvement en raffinerie et l'analyse au laboratoire. Or, l’étude bibliographique a montré que certaines espèces silicées réactives issues de la dégradation du PDMS, notamment dans l'environnement, pouvaient évoluer au cours du temps. Dans ce cas, les molécules silicées retrouvées dans les échantillons analysés ne sont pas forcément celles présentes au moment de l’empoisonnement des catalyseurs. De plus, les conditions appliquées dans les procédés de raffinage sont très loins de celles étudiées pour la dégradation du PDMS dans la littérature. En effet, la présence de radicaux carbonés issus du craquage thermique des hydrocarbures permet d'émettre l'hypothèse d'une réactivité avec les produits de dégradation du PDMS formés. La présence de vapeur d'eau, notamment dans le procédé de vapocraquage, est également un facteur qui peut influencer la nature chimique des composés silicés produits. Afin de répondre à ces différentes hypothèses, la partie C s'intéressera à la représentativité des échantillons produits au moyen d'une expérimentation pilote et à leur analyse grâce à la combinaison de plusieurs techniques analytiques présentées précédemment.

Partie C. Analyse d'échantillons représentatifs

Introduction

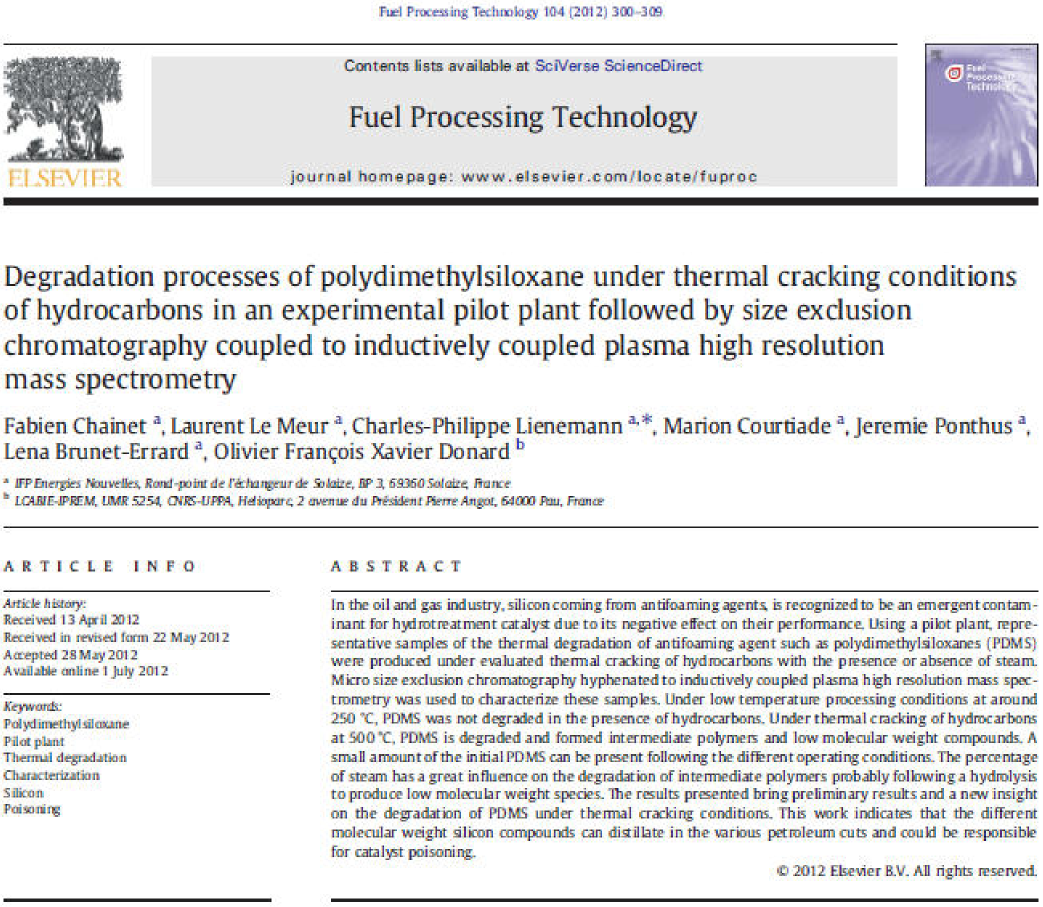
Cette troisième partie a pour but de décrire la production des échantillons « frais » et représentatifs de la dégradation d'un agent antimousse mises en place au cours de mon travail de thèse dans des conditions similaires à celles appliquées dans les procédés de raffinage. La caractérisation de ces échantillons, effectuée grâce aux outils analytiques développés dans la partie B est également présentée.

La réaction de dégradation du polydiméthylsiloxanes (PDMS) a été effectuée en présence d'hydrocarbures et de vapeur d'eau à différentes teneurs en faisant également varier les temps de séjours. L'objectif est de s'affranchir des concentrations traces et de la complexité des matrices pétrolières qui rendent complexe l'accès à la caractérisation des composés silicés par leur structure chimique. Les conditions de température et la variation du temps de séjour vont donc probablement entraîner la formation d'une multiplicité de produits de dégradation du PDMS mais également de nombreux produits de craquage des hydrocarbures. Il sera donc intéressant d'observer l'influence des conditions de craquage thermique sur la nature des produits formés par rapport aux travaux de la littérature. Après condensation des vapeurs produites lors de la réaction, une fraction gazeuse et une fraction liquide sont collectées en sortie de l'unité pilote, stockées de manière à conserver l'intégrité de l'échantillon puis analysées. La démarche analytique incluant le prélèvement, la conservation et l'analyse de ces deux fractions est cruciale pour s'assurer de la représentativité de la spéciation et minimiser de l'évolution des espèces silicées. Cette partie est divisée en trois chapitres.

Dans un premier temps, le Chapitre 6 est entièrement consacré à la description de l'expérimentation de dégradation du PDMS à haute température effectuée sur une unité pilote et à la caractérisation de façon macroscopique des échantillons liquides par µSEC-ICP/HRMS. Ce travail a été publié dans **Fuel Processing Technology** (Fuel. Process. Technol.) en 2012. Le choix des conditions opératoires est clairement exposé afin de déterminer l'influence de la température, des temps de séjour ou de la teneur en vapeur d'eau sur la dégradation du PDMS et surtout sur la formation des produits de dégradation. Afin de s'assurer du craquage thermique des hydrocarbures, la GC-FID a permis de quantifier les différents produits issus du craquage du mélange heptane/xylène choisi comme source initiale d'hydrocarbures. Un suivi par Fluorescence par rayons X (XRF) a été également effectué pour s'assurer de l'équilibre de la réaction de dégradation lors du prélèvement. La masse moléculaire du PDMS au cours de ces tests de dégradation a été suivie par une méthode µSEC-ICP/HRMS qui permettra également de déterminer la répartition du silicium selon les différentes distributions moléculaires obtenues. Une comparaison entre les concentrations en silicium total mesurées par XRF et par µSEC-ICP/HRMS a également été effectuée.

Dans un second temps, l'objectif principal sera de caractériser les composés silicés de bas poids moléculaire qui s'avèrent être les composés les plus à même d'affecter les catalyseurs d'HDT. Le Chapitre 7 est consacré à l'analyse de la fraction gazeuse d'une part (Section 7.1) et de la fraction liquide d'autre part (Section 7.2) issues des échantillons de dégradation du PDMS. Ce chapitre est basé sur l'écriture de deux articles (**Part 1-Gas fraction** and **Part 2-Liquid fraction**) soumis dans le journal **Fuel**. Après optimisation de la méthode sur des molécules modèles, la fraction gazeuse a été caractérisée par GC/TOFMS équipée d'une vanne cryogénique. Le but est de déterminer la présence potentielle de composés silicés volatils, pouvant distiller dans les coupes gaz C_1-C_4 et empoisonner les catalyseurs. Concernant la fraction liquide, une approche multi-technique basée sur les développements précédents a été mise en place pour essayer de parvenir à la caractérisation moléculaire de cette fraction (Section 7.2). En effet, seule l'association des différents résultats fournis par chaque technique appliquée devrait permettre d'approcher la structure chimique des molécules silicées formées. La GC/MS SIM a tout d'abord été appliquée pour la spéciation des composés silicés connus tels que les siloxanes cycliques et linéaires et les α,ω-dihydroxy polydimethylsiloxanes. La GC-ICP/MS a été utilisée pour déterminer les temps de rétention des composés silicés inconnus pour ensuite obtenir leur spectre de masse par GC-GC/TOFMS. Néanmoins, certains développements supplémentaires sont nécessaires pour abaisser les limites de détection actuelles et progresser sur l'aspect quantitatif (Section 5.1). La GC/TOFMS et la GC-GC/TOFMS ont respectivement été appliquées pour obtenir les spectres de masse des composés silicés en impact électronique (information sur la fragmentation de la molécule) et en ionisation chimique (accès à la masse moléculaire). En raison du faible nombre de standards silicés disponibles et du faible nombre de spectres de masse présents en bibliothèque et coïncidant avec ceux obtenus par TOFMS, la caractérisation structurale des composés silicés s'avère très complexe. Néanmoins, la FT-ICR/MS permet l'obtention de la formule brute des composés silicés ainsi que leur nombre d'insaturations. Nous verrons donc dans cette section comment l'approche que nous avons mise en place en associant les résultats obtenus par les différentes techniques peut permettre d'accéder à une caractérisation structurale des espèces silicées. Le potentiel de la MS^n afin de renforcer le choix des structures proposées a également été abordé. Les différentes molécules caractérisées sont discutées selon leur concentration relative et leurs conditions de formation.

Chapitre 6. Degradation processes of polydimethylsiloxane under thermal cracking conditions of hydrocarbons in an experimental pilot plant followed by size exclusion chromatography coupled to inductively coupled plasma high resolution mass spectrometry



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Degradation processes of polydimethylsiloxane under thermal cracking conditions of hydrocarbons in an experimental pilot plant followed by size exclusion chromatography coupled to inductively coupled plasma high resolution mass spectrometry

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ABSTRACT

In the oil and gas industry, silicon coming from antifoaming agents, is recognized to be an emergent contaminant for hydrotreatment catalyst due to its negative effect on their performance. Using a pilot plant, representative samples of the thermal degradation of antifoaming agent such as polydimethylsiloxanes (PDMS) were produced under evaluated thermal cracking of hydrocarbons with the presence or absence of steam. Micro size exclusion chromatography hyphenated to inductively coupled plasma high resolution mass spectrometry was used to characterize these samples. Under low temperature processing conditions at around 250 °C, PDMS was not degraded in the presence of hydrocarbons. Under thermal cracking of hydrocarbons at 500 °C, PDMS is degraded and formed intermediate polymers and low molecular weight compounds. A small amount of the initial PDMS can be present following the different operating conditions. The percentage of steam has a great influence on the degradation of intermediate polymers probably following a hydrolysis to produce low molecular weight species. The results presented bring preliminary results and a new insight on the degradation of PDMS under thermal cracking conditions. This work indicates that the different molecular weight silicon compounds can distillate in the various petroleum cuts and could be responsible for catalyst poisoning.

6.1 Introduction

Silicon speciation is of great interest in the oil and gas industry due to the negative effect of silicon compounds on the performance of catalysts. In the petroleum industry, silicon mainly originates from the use of antifoaming such as polydimethylsiloxanes (PDMS) to avoid the formation of emulsions in different processes such as coking, visbreaking, steamcracking or distillation [4, 5, 30, 50]. It is also used to enhance the crude oil recovery from the reservoir and always appear in the crude oil and the final products [5].

PDMS, has a structural unit of $–(CH_3)_2$-Si-O- and displays excellent properties of low surface tension and initial great thermal stability [7]. Under the high temperature applied during thermal cracking processes, PDMS will degrade around 300°C [10, 13] and will generate many different silicon species in the final petroleum products that can affect the performance of catalyst. PDMS degradation is well known and has been previously investigated [10, 11, 13]. Indeed, the thermal degradation of PDMS under inert gas was largely reported in the literature yielding cyclic siloxanes (D_n) as the major degradation products [14]. However, no studies exist under real thermal cracking conditions at high temperature and especially in the presence of hydrocarbons and in the presence or absence of steam. There is therefore a clear need to identify the chemical nature of PDMS degradation silicon species in petroleum products and their relative concentration due to their poisoning effects under “real conditions”. Previous results have demonstrated that these effects depends on the catalyst [32], on the operating conditions [45] and more especially on the nature of silicon molecule [49].

Up to now, these issues have being mainly achieved and monitored using total silicon determination [14]. However, the complexity of petroleum matrices combined to the trace levels of silicon and potential contamination problems, have considerably hampered the development of analytical methods for silicon speciation [14]. Very few studies have been reported concerning the determination of silicon species in petroleum products [18, 279, 303]. Low molecular weight (LMW) silicon species were identified by GC/MS SIM and around 50% of the total silicon content were quantified in gasolines [18]. Very novel results and advances using a novel method by ESI-FT-ICR/MS combined to Kendrick plots, have shown that new silicon species with unsaturations could be characterized in petroleum products [279]. When dealing with high molecular weight (HMW) silicon polymers such as PDMS, size exclusion chromatography (SEC) coupled to an element specific detection such as inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP/MS) appears to be a versatile tool for the characterization of silicon polymer such as PDMS [14]. The recent use of ICP/MS has allowed to gain an increase in sensitivity for the detection of PDMS respectively in xylene [203] and in crude oil [303]. However, it is necessary to use a resolution at around 2,000 to avoid spectral interferences for silicon [170]. In organic matrices, such as petroleum products, the main interference on ^{28}Si (m/z 27.97638) consists in the formation of carbon monoxide ($^{12}C^{16}O$, m/z 27.99437) in the plasma [136]. Moreover, differences on the ICP signal response for silicon species was previously demonstrated by Sanchez *et al.* [165] but could be minimized using specific nebulisation systems [166, 278] or by developing a specific quantification methods with several silicon standards. Therefore, silicon speciation using ICP/MS in a complex matrix appears as a great analytical challenge.

Regarding the instability and the reactivity of several silicon compounds [84], the chemical nature of silicon species affecting the catalytic processes can be modified prior to the analysis and hence the previous results reported may be affected by the instability of the silicon species collected. The identified silicon species after several weeks or months from the initial sampling may be different compared to the initial silicon molecules that can affect the catalytic processes. PDMS used as antifoaming in refining processes or its degradation products can react with the hydrocarbon matrix and generates new unknown silicon degradation products. Therefore, beyond the direct analytical difficulty, the collection and storage of the samples are critical for a representative assessment of silicon speciation in petroleum products. To overcome this serious challenge, the production of fresh and representative samples of the degradation of PDMS in the presence of hydrocarbons under thermal cracking conditions and their direct analysis is necessary.

The aim of this study is to improve the knowledge of direct silicon speciation in the oil and gas industry for an improved understanding of catalyst poisoning conditions. In this paper, we present the production of petroleum samples representative of realistic PDMS degradation under thermal cracking of hydrocarbons. This project uses an experimental pilot plant especially modified for this work at IFPEN. Heptane and xylene were chosen to be the initial source of hydrocarbons. Five samples were produced under thermal cracking conditions at 500°C with different residence times and steam content to evaluate the conditions applied in refining processes such as visbreaking, coking or steam cracking. During the process, these samples were collected and then carefully stored in liquid nitrogen at -195°C to avoid the evolution of silicon species and to allow further later representative characterization of the samples. GC-FID was used to verify the conversion of hydrocarbons during the process. After calibration of a µSEC-ICP/HRMS method and its validation with PDMS and silicon standards, the method was applied to the five samples to evaluate the degradation behaviour and pathways of PDMS in these conditions at a macroscopic scale. The quantification obtained by µSEC-ICP/HRMS was also compared to XRF measurements to be consistent with the total silicon content.

6.2 Materials and Methods

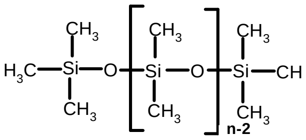
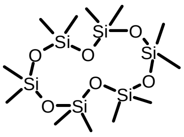
6.2.1 Silicon standards and solutions

Two polydimethylsiloxanes (PDMS) at 60,000 and 12,500 cSt, two PDMS with low viscosity (2 and 0.65 cSt) and one cyclic siloxane (D_6) were purchased from Sigma-Aldrich (Lyon, France). Others PDMS with different viscosities (1,000; 100; 20 and 3 cSt) were supplied by Bluestar Silicones (Saint Fons, France). These silicon standard molecules were used for the mass calibration of µSEC-ICP/HRMS with molecular masses ranging from 162 to 116,500 g.mol^{-1}. Table 6-1 presents the abbreviations and the different chemical properties (viscosity, degree of polymerization, molecular mass and chemical structure).

For the analytical steps, tetrahydrofuran (THF) of ULC-MS grade was obtained from Biosolve Chemicals (Valkenswaard, Netherlands). Heptane (AnalaR Normapur, 99.7%) and xylene containing a mixture of the three isomers (ortho, metha and para-xylene) (Purex, 98.5%) were respectively purchased from VWR (Fontenay sous Bois, France) and Carlo-Erba (Val De Reuil, France).

Each molecule (Table 6-1) was prepared at an initial concentration of 1000 mg.kg^{-1} of Si in THF and different dilutions were performed to evaluate the limits of detection (LOD$_s$) and the linearity of the ICP response. Solutions and standards were stored in 30 ml high density polyethylene bottles (VWR, Fontenay sous Bois, France) at 4°C. Prior to analysis, the samples were transferred in polypropylene vials with septa only made of PTFE, provided by VWR (Fontenay sous Bois, France) in replacement of classical septa made of silicones to avoid possible contaminations [14].

Table 6-1. Silicon molecules properties

Molecules Abbreviations	Degree of polymerization n	Viscosity (cSt)	Medium Molecular masses (g.mol^{-1})	Chemical structure
Polydimethyl siloxanes PDMS	1,500	60,000	116,500	
	900	12,500	67,700	
	500	1,000	39,000	
	150	100	11,000	
	40	20	3,000	
	7	3	548	
	5	2	385	
	2	0.65	162	
Dodecamethyl-cyclohexasiloxane D_6	6	4.5	444	

6.2.2 Pilot plant design and use for representative samples production

6.2.2.1 *Design of the pilot plant*

In order to obtain the best representative samples, the PDMS degradation experiments were performed in a pilot plant used for petroleum thermal studies at IFPEN. This pilot plant initially contained the oven stage and the steam generator with a tank. The system was adapted to our study and deeply modified to study the PDMS degradation under thermal cracking conditions and to characterize silicon degradation compounds [304] (Figure 6-1).

Three tanks were used for the storage of the different products (heptane, xylene, water and PDMS in solution). Heptane and xylene with a mixture 50:50 in volume as source of hydrocarbons were supplied by a Bischoff pump (Bischoff, Leonberg, Germany). Heptane and xylene were chosen because it was a simple mixture of representative hydrocarbons present in gasoline. Hydrocarbons and water were mixed in a static stirring after being vaporized respectively by heating tracers and steam generator (Figure 6-1). The system was equipped with a HPLC pump Perimax (Spetec Analab, Bishheim, France) for supplying PDMS dissolved in heptane and xylene. This solution was injected in a glass pneumatic concentric nebulizer (TR-30-A1, Meinhard Glass Products, Golden, Colorado, USA) with the addition of nitrogen in order to pre-vaporize the effluents in the reactor head (12 cm of length and internal diameter of 20 mm) and avoid overpressure in the reactor. PDMS in heptane and xylene (50:50) with different percentages of steam was heated in a tubular reactor applying different residence times and containing honeycomb stitches. The dimensions of the reactor were as follows: 87.5 cm of length with i.d. of 20 mm. The honeycomb stitches, made of cordierite, were totally inert and allowed a better contact during the reaction of PDMS thermal degradation. Finally, the vapour degradation products were cooled and condensed with a cooling group set at 0°C to separate gas and liquid fraction of each effluent (Figure 6-1 and Figure 6-2). During the production of samples, X-ray Fluorescence analysis was performed to monitor the total silicon concentration in the liquid fraction for the determination of the reaction equilibrium (Figure 6-2).

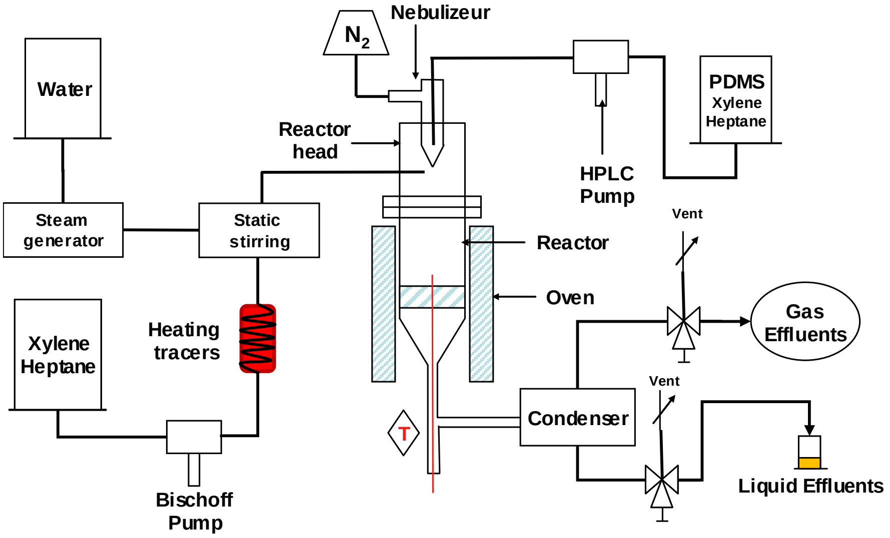


Figure 6-1. Scheme of the pilot plant performed for the production of degradation samples

6.2.2.2 Operating conditions of the pilot plant

The operating conditions were chosen to evaluate thermal cracking processes such as coking or visbreaking [36] and steam cracking processes [39, 40] where PDMS is usually added prior to these processes [14]. Coking and visbreaking are two main conversion processes to thermally crack at 500°C heavy products into lighter cuts (diesel or gasoline) [36]. The long residence times applied in these processes can range from 1 to 3 minutes and up to 24 hours. These time conditions were respectively applied to visbreaking and to coking processes. Steam cracking is also a key process for the production of light petroleum products (C_2-C_4 and BTX; benzene, toluene and xylene) at 800°C under evaluated steam conditions and with short residence times (0.1 and 1.2 seconds) [39]. The steam content clearly depends on the molecular mass of the hydrocarbons and the percentage is generally ranging from 20 and 100 in mass of steam per mass of hydrocarbon [39]. The design of the pilot plant and the safety conditions needed, introduced some differences with respect to the real thermal cracking processes. It was impossible to heat at 800°C without the formation of coke in our conditions and to apply very long residence time.

In our case, the thermal cracking conditions were performed at 500°C, in the presence of steam and with residence times ranging from 0.5 seconds (short residence time) up to 5 seconds (long residence time). The residence time was calculated as the ratio between the volume of the reactor multiplied by the bed porosity and the inlet gas flow multiplied by the temperature [305]. This temperature is considered to be the reference temperature for the majority of thermal cracking processes [36]. These conditions were used to evaluate the real operating conditions taking place during thermal cracking and to study the influence of the residence time and the steam content on PDMS thermal degradation in the presence of hydrocarbons under simulated refining conditions. The different degradation tests and their relative conditions are illustrated in Table 6-2. All tests presented here were achieved with PDMS 60,000 cSt because it is the most employed antifoaming in the oil and gas industry [5, 30]. However, PDMS 12,500 cSt was also evaluated under the conditions of the tests D and E (Table 6-2) but no significant differences on molecular distributions of degradation products between the two PDMS were observed.

Table 6-2. Operating conditions of the process for all produced samples

Tests	Temperature (°C)	Residence time (s)	Steam (%m)	Concentration (mg.kg^{-1} of Si)
A	250	long (5.50 s)	0%	1164±70
B	500	short (0.64 s)	50%	2482±155
C	500	short (0.49 s)	13%	1342±53
D	500	long (3.48 s)	10%	1571±48
E	500	long (3.50 s)	0%	1129±83

Similarly to a low temperature process in the oil and gas industry, the test A was achieved at 250°C with a long residence time in the absence of steam to study the PDMS stability. The polymer should not degrade at this temperature [10, 11, 13]. Four other experiments were performed at 500°C. To obtain samples evaluating coking or visbreaking conditions, a long residence time was used for the test E without steam. Test D respectively with 10% of steam in mass was also achieved during this work to determine the influence of steam under long residence time (tests D and E). Short residence times for the tests B and C with respectively 50% and 13% in mass of steam per mass of hydrocarbons were applied to evaluate steam cracking conditions at 500°C. These conditions allowed the determination of the influence of the residence time (tests C and D) and steam content (tests B and C) on PDMS degradation under thermal cracking.

During the total silicon analysis, only the yield of silicon in the liquid fraction was calculated by the ratio between the mass of PDMS injected per minute and the concentration of silicon (mg of Si per minute) measured by XRF at the end of the sample production. All tests have presented a recovery ranging from 74 and 85% and indicated that the majority of silicon initially injected through PDMS was recovered after the thermal degradation in the liquid fraction.

To control the quality of the process and due to the severe analytical constraints, the pilot plant was cleaned with the same mixture of heptane and xylene at high flow rate between each thermal degradation test of PDMS. After these steps, a blank was performed in the same conditions of the degradation test and was analyzed by XRF to be sure that no residual silicon (<1% of the total silicon) was present (Table 6-2).

6.2.3 Analytical strategy for the effluents characterization

To understand the PDMS degradation under thermal cracking and to characterize the different degradations products, a multi-technical approach was previously developed [18, 279] and applied to the effluents. The flow chart of the operation, sample collection and storage and analytical conditions is highlighted in Figure 6-2. Due to the possible evolution of silicon species over time during storage, the sampling and the sample storage steps were critical prior to the analysis. At the end of the reactor, the vapour of the degradation products were condensed. The gas and the liquid phases were then separated and sampled (Figure 6-2). The gas fraction was collected in Tedlar bags of 1L with polypropylene valve (Interchim, Montluçon, France), immediately analyzed by GC/TOFMS using a cryogenic valve and finally stored at 4°C in a refrigerator (results will be presented elsewhere). The liquid fraction was collected in two different 30 ml high density polyethylene (HDPE) bottles. This fraction was directly analyzed by XRF to determine total silicon and by GC-FID to identify the hydrocarbons produced by the thermal cracking of heptane and xylene. The remaining part was stored at 4°C in a fridge respectively for later µSEC-ICP/HRMS analysis to study the HMW silicon degradation compounds and for others analysis by GC/MS and FT/MS to obtain a molecular characterization of the LMW degradation products (Figure 6-2). The liquid fraction contained in the second HDPE bottle was directly transferred in cryogenic tubes (Fisher Scientific, Illkirch, France) and stored using liquid nitrogen (-195°C) in a dewar in order to minimize the possible evolution of silicon species. These careful storage conditions of the samples allowed the same analysis previously detailed by µSEC-ICP/HRMS for HMW compounds and by GC/MS and FT/MS for LMW molecules (Figure 6-2). The comparison of the analysis respectively stored at 4°C (classical storage for a gasoline coming from a refinery) and at -195°C will bring crucial information about the potential evolution of silicon species.

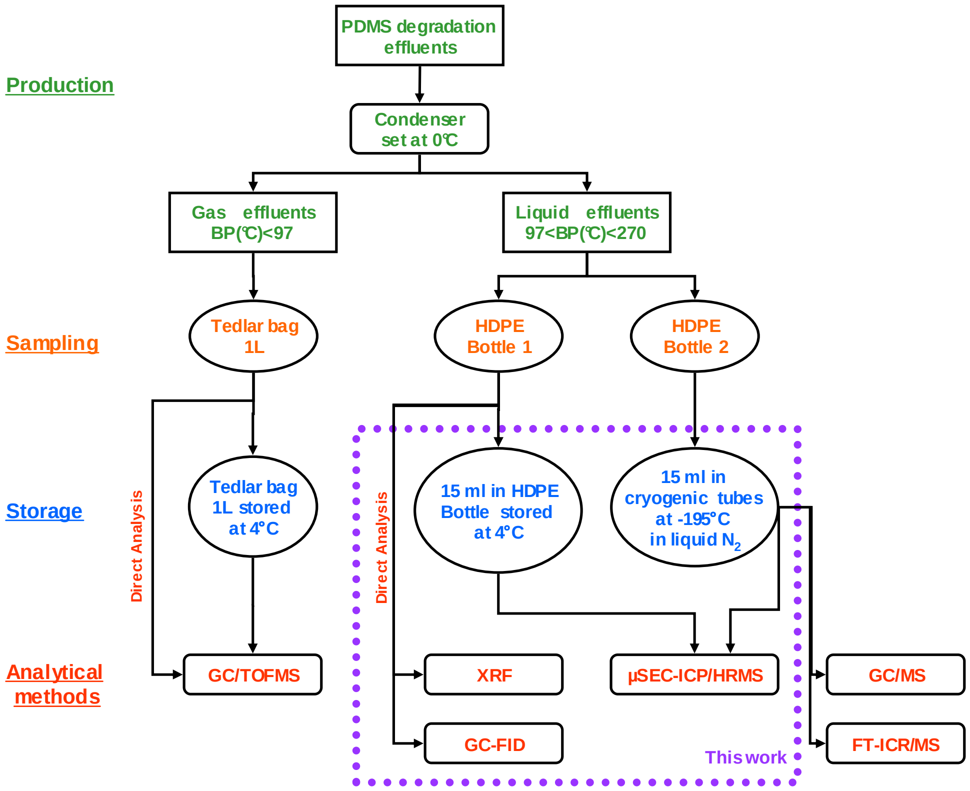


Figure 6-2. Flow chart of the analytical strategy for the effluent characterization

6.2.3.1 X-Ray Fluorescence

Total silicon concentration was determined by Wavelength Dispersive X-ray Fluorescence to follow the reaction equilibrium. All measurements were conducted using an Axios X-ray fluorescence spectrometer (XRF) (PANalytical, Eindhoven, the Netherlands), operating at 125 mA and 32 kV and equipped with an automatic sample changer. Samples were contained in 32 mm diameter cells with 6µm polypropylene support film as the cell window. The measurements were performed under an helium atmosphere using a chrome (Cr) target tube.

6.2.3.2 GC-FID

To obtain the conversion of heptane and xylene used as hydrocarbon source, the detailed analysis of hydrocarbons was performed using an Agilent 6890 gas chromatograph (Agilent Technologies, Massy, France) following the ASTM D6733 method [261]. The injection was made at 250°C with a 1:200 split ratio and an injection volume of 0.5 µl. The separation was performed with a 50 m PONA column (0.20 mm i.d., 0.50 µm film thickness) from J&W Scientific (Folsom, California, United States). The oven temperature ramp varied from 35°C to 114°C at 1.1°C.min^{-1} and then from 114 to 280°C at 1.7°C.min^{-1}. Helium (99.99% Air liquide, France) was used as a carrier gas with a constant pressure of 105 kPa. Analytes were detected with a flame ionization detector (FID) at 320°C.

6.2.3.3 µSEC-ICP/HRMS

All samples were analyzed with a Dionex (Amsterdam, The Netherlands) UltiMate 3000 HPLC system hyphenated to a Thermo Scientific Element XR sector-field-ICP MS instrument (Thermo Fisher, Bremen, Germany). Chromatographic separations were performed using two Shodex (Showa Denko, Japan) micro-type styrene–divinylbenzene gel permeation columns (0.1 mm i.d. x 250 mm length) connected in series: KF404-1E (particle size: 3 µm, exclusion limit: 400,000 Da) and KF402-1E (particle size: 3 µm, exclusion limit: 5,000 Da). After dilution to obtain a total silicon concentration of 50 mg.kg^{-1}, a volume of 1 µl of each sample was isocratically eluted in tetrahydrofuran as the mobile phase at a flow rate of 13 µ. min^{-1}. The total run time was 120 minutes.

The µSEC-ICP/HRMS was calibrated in mass by analysing six PDMS and three silicon compounds with molecular masses ranging from 162 g.mol^{-1} to 116,500 g.mol^{-1} (Table 6-1). The operating conditions and the measuring parameters applied to the ICP-HR/MS instrument were set to provide the highest most stable and reproducible response. These conditions are given in Table 6-3 and were previously described in more details in Pohl *et al.* [303]. The ICP/HRMS was operated at a medium resolution of 4,000 in order to avoid the spectral interferences on silicon isotopes [136] and more specifically on ^{28}Si by N_2 ($^{14}N^{14}N^+$) and by CO ($^{12}C^{16}O^+$) [254]. ^{13}C isotope was monitored to control the stability of the plasma during the continuous introduction of petroleum samples. The acquisition of µSEC-ICP/HRMS signals was achieved in the time-resolved mode. A built-in software application was used to integrate the signal recorded on ^{28}Si for the determination of the LOD$_s$ and the calibration curve.

Table 6-3. ICP/HRMS operating conditions

RF Power	1500W
Plasma gas flow rate	16.00 $l.min^{-1}$
Auxiliary gas flow rate	0.80 $l.min^{-1}$
Nebulizer gas flow rate	0.51 $l.min^{-1}$
O_2 gas flow	0.08 $l.min^{-1}$
Carrier stream/mobile phase flow rate	13 $\mu l.min^{-1}$
Detection mode	Triple: counting, analog, faraday
Isotopes measured	^{13}C, ^{28}Si, ^{29}Si, ^{30}Si
Number of points per peak	20
Dwell time per point	60
Integration type	Average

6.3 Results and Discussion

Under these model experimental conditions evaluating the thermal cracking of hydrocarbons, the PDMS degradation was followed using a multi-technical approach (Figure 6-2). Hydrocarbons were characterized by GC-FID to evaluate the conversion of heptane and xylene under thermal cracking conditions at 500°C. The µSEC-ICP/MS method was validated to allow a mass calibration with PDMS and a quantification of silicon through the different elution areas of the PDMS degradation products. Total silicon measured by XRF was recovered by µSEC-ICP/HRMS with a percentage ranging from 84 to 99%. The medium molecular mass and the relative concentration of the PDMS degradation products obtained under the different conditions were discussed according to the temperature, the residence time and the steam content for the five degradation studies (Table 6-2).

6.3.1 Conversion of hydrocarbons

GC-FID measurements were firstly used to analyse the conversion of heptane and xylene initially present as source of hydrocarbons during the thermal degradation process. At 250°C, heptane and xylene are not cracked. At 500°C, the percentages of conversion obtained ranged from 10 to 22% for heptane and from 3 to 13% for xylene at 500°C following the different operating conditions of residence times and steam. Under evaluated coking of visbreaking conditions (test E: 500°C, without steam and long residence time), paraffins (40.8%), naphthens (0.1%), aromatics (58.9%) and olefins (0.2%) were identified by GC-FID, with the composition ranging from 1 to 15 carbon atoms. Using steam and short residence time, hydrocarbons are less cracked but reactive carbon radicals are also formed. The complexity of the hydrocarbons generated demonstrates the presence of numerous carbon radicals produced during the thermal cracking at 500°C of the initial mixture only containing heptane and xylene. These results showed that our operating conditions correctly evaluate the thermal cracking of hydrocarbons. Hydrocarbon radicals, especially coming from aromatics and olefins, can react with PDMS degradation products and form a wide array of new unknown silicon compounds, similarly to what can happen in real refining processes. These likely new unknown silicon species will be presented and discussed in further papers.

6.3.2 Validation of the µSEC-ICP/HRMS method

6.3.2.1 PDMS mass calibration

The µSEC-ICP/HRMS method was applied to observe the PDMS degradation at a macroscopic scale. Various PDMS standards with different molecular masses ranging from 162 to 116,500 g.mol^{-1} and one cyclic siloxane standard (D_6) were separately analyzed in THF at a concentration of 20 mg.kg^{-1}. The chromatograms of these different PDMS standards are presented in Figure 6-3. This figure illustrates the overlay of the chromatograms obtained for the six polymers in solid line and for the three LMW compounds in broken line obtained by µSEC-ICP/HRMS. LMW silicon compounds (L_2, L_5 and D_6) are single oligomers and consequently resulted in sharp peaks. PDMS containing a distribution of molecular masses resulted in much broader peaks.

A good separation was obtained for almost polymers and especially for low molecular silicon compounds due to the choice of the two µ-columns. The small difference in molecular mass between L_5 (384 g.mol^{-1}) and D_6 (444 g.mol^{-1}) does not allow the separation by µSEC but L_2 (162 g.mol^{-1}) and D_6 (444 g.mol^{-1}) as LMW silicon compounds, are correctly separated. PDMS 60,000 and 12,500 cSt are not clearly separated under these conditions but they are not used simultaneously in the tests. Moreover, it was known that LMW silicon compounds have a bigger influence than HMW molecules on catalyst poisoning [14].

The µSEC-ICP/HRMS analysis of six PDMS standards and L_2 allowed the mass calibration of the µSEC method to determine the medium molecular mass of silicon polymer in the PDMS degradation samples. A linear relation between the logarithm of the medium molecular mass (MM) and the retention times (t_R) with a correlation coefficient of 0.9976 was established: $\log(MM) = -0.0089t_R + 13.577$. The range of molecular mass was indicated in Figure 6-3 and in Figure 6-5 for a better visualization.

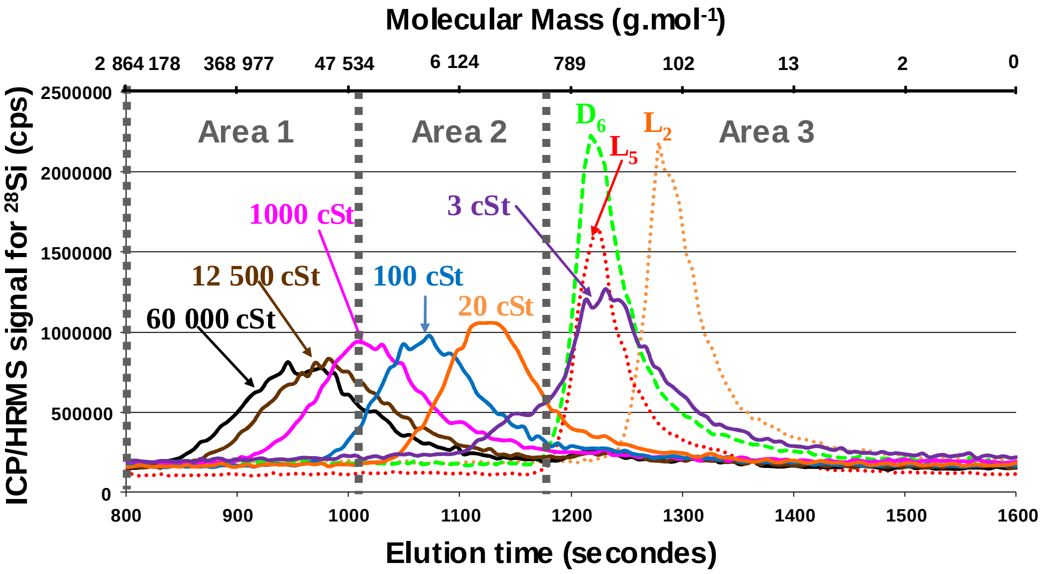


Figure 6-3. Overlay of the µSEC-ICP/HRMS chromatograms for six PDMS standards and three LMW silicon model compounds injected at 20 mg.kg^{-1} in THF. Three elution areas (1, 2 and 3) were defined for the quantification method

6.3.2.2 Quantification method

The chromatograms shown in Figure 6-3 clearly indicate that the peak area signal was not universal for silicon as might be expected using ICP/MS detection [203]. The dependence of the ICP signal with the chemical form of silicon species was previously described in the literature [165-167, 203, 278]. Due to the different response on ICP signal for silicon compounds, a quantification method was developed using calibration curves based on the different elution areas of the different PDMS standards (Figure 6-3).

The LOD$_s$ (limits of detection) and LOQ$_s$ (limits of quantification) were calculated considering a signal to noise of 3 and 10 respectively for standard compounds in THF at a concentration of 20 mg.kg^{-1} (Table 6-4). The use of an injector and a torch made of quartz involves a high background of silicon. Quantification limits are ranged from 2 to 5 mg.kg^{-1} for all silicon standards and are sufficient to analyse all degradation samples regarding the total silicon content (Table 6-2).

Elution areas were determined after the µSEC-ICP/HRMS analysis of the degradation samples. The calibrations were linear (R > 0.998) from 5 to 100 mg.kg^{-1} for the two PDMS (60,000 and 20 cSt) and for D$_6$ which are chosen here as references for the quantification method (Table 6-4). This method is extrapolated from the use of the calibration curve generated with the silicon standard, which eluted in each elution area (Figure 6-3 and Figure 6-5). Table 6-4 presents the different calibration curves of silicon standard per elution area previously defined in Figure 6-3. For the quantification, PDMS 60,000 cSt calibration curve was applied to area 1. Intermediate polymer 20 cSt was principally eluted in area 2 and its calibration curve was applied to this area. The quantification for eluted peaks in area 3 was achieved by the calibration curve of D_6.

Table 6-4. Validation data of the µSEC-ICP/HRMS method for the three silicon standards

Molecules	LOD	LOQ	Area 1		Area 2		Area 3	
	mg.kg^{-1}		$y_1=a_1x+b_1$	R_1^2	$y_2=a_2x+b_2$	R_2^2	$y_3=a_3x+b_3$	R_3^2
PDMS 60,000 cSt	1.2	3.2	$4.32\ 10^6x-12.99\ 10^3$	0.998	n.c.	--	n.c.	--
PDMS 20 cSt	1.5	5.0	n.c.	--	$4.99\ 10^6x-12.62\ 10^6$	0.999	n.c.	--
D_6	0.8	2.7	n.c.	--	n.c.	--	$7.92\ 10^6x-15.02\ 10^6$	0.999

n.c. Equations not considered for the quantification

6.3.3 Total silicon concentration

The concentration of total silicon respectively obtained by µSEC-ICP/HRMS and by XRF were compared in order to evaluate the total silicon content. Table 6-5 lists the different concentrations of silicon in mg.kg^{-1} obtained by the two techniques for all investigated samples. For all degradation samples, 84 to 99% of the total silicon content immediately measured after the production by XRF is quantified by µSEC-ICP/HRMS (Table 6-5). The differences on total silicon concentration for test A and test C can be explained by the possible volatilization of light hydrocarbon compounds in the XRF cell during the analysis. Moreover, due to the non universal response for silicon observed by ICP/HRMS (Figure 6-3), the total silicon concentration in the area 3 was calculated by the calibration curve of D_6 (Table 6-4). The peak eluted in area 3 contained a distribution of different silicon compounds with an ICP response potentially different than for D_6 considered as the reference compound for the calibration of the entire area 3. The quantification method minimized the difference on the ICP response for silicon compounds but could not totally avoid the discrimination. However, the percentages of recovery between XRF and µSEC-ICP/HRMS confirmed that the µSEC-ICP/HRMS allowed the speciation of silicon in all investigated PDMS degradation samples and can be easily applied in petroleum products such as crude oil or heavy distillation fractions.

Table 6-5. Silicon concentration measured by XRF and by µSEC-ICP/HRMS in mg kg^{-1} and in percentage for all samples

Tests		PDMS	Test A	Test B	Test C	Test D	Test E
Area 1	C (mg.kg^{-1})	n.c.	432±5	431±5	132±2	107±1	115±1
	%	46	45	16	12	8	9
Area 2	C (mg.kg^{-1})	n.c.	469±4	849±7	454±3	390±1	531±2
	%	49	49	32	43	28	46
Area 3	C (mg.kg^{-1})	n.c.	64±1	1375±10	479±4	898±7	521±4
	%	5	6	52	45	64	45
Total Area	C (mg.kg^{-1})	n.c.	965±16	2655±43	1065±14	1395±19	1167±17
XRF	C (mg.kg^{-1})	n.d.	1164±73	2482±155	1342±85	1571±48	1129±83
Total Si content	%	n.c.	89	99	84	93	98

n.d. and n.c. respectively for not determined and not calculated

6.3.4 Characterization of PDMS degradation samples

This part presents the five PDMS 60,000 cSt degradation studies in the presence of hydrocarbons according to the applied temperature (250°C and 500°C). Under thermal cracking of hydrocarbons at 500°C, the influence of the residence time (short and long) and the steam content were respectively discussed. Three elution areas relative to the initial PDMS, intermediate polymers and LMW compounds were characterized following the different operating conditions and will be further developed in this section. The medium molecular mass of all elution areas were determined using the PDMS mass calibration and the total silicon was measured using the quantification method by µSEC-ICP/HRMS.

The µSEC-ICP/HRMS method was applied to the degradation samples stored at 4°C in the refrigerator and at -195°C in liquid nitrogen to control the possible evolution of silicon species. Figure 6-4 presents the two µSEC-ICP/HRMS chromatograms of the test E after a storage in the refrigerator (a) and in liquid nitrogen (b). No difference on the medium molecular masses of the three elution areas were observed between samples stored in a refrigerator and samples stored in liquid nitrogen (Figure 6-2). A small difference around 10% on the area 3 was observed using the quantification method. This insignificant difference may be due to the volatilization of light hydrocarbons in the samples stored in the refrigerator that can increase the concentration of silicon in this elution area. Thus, only the results on samples stored in liquid nitrogen more representative of the "real conditions" are presented in this paper. The possible evolution on silicon species between different storage conditions essentially concerns LMW silicon compounds eluted in the area 3 that can be characterized by other techniques (GC/MS [18] and FT-ICR/MS [279]) (Figure 6-2).

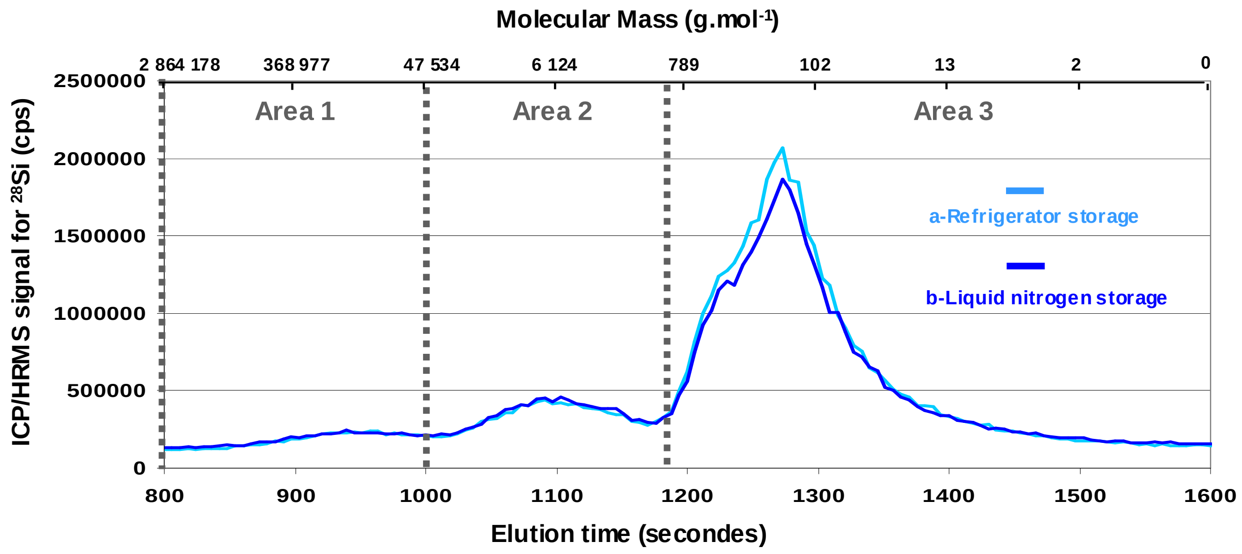


Figure 6-4. µSEC-ICP/HRMS chromatograms obtained for the degradation test E, performed at 500°C with a long residence time (3.50 s) and without steam, respectively stored in the refrigerator at 4°C (a) and in liquid nitrogen (b) at -195°C

For all other samples stored in liquid nitrogen at -195°C, Figure 6-5 summarizes the µSEC-ICP/HRMS chromatograms for the five investigated samples and their relative operating conditions (Table 6-2). PDMS 60,000 cSt, D_6 and L_2 chromatograms are also overlaid in this figure to compare the molecular mass of degradation products with known silicon compounds. The quantification results are presented in Table 6-5. For a better visualization, Figure 6-6 displays the percentage of silicon concentration per elution area relative to the concentration values indicated in Table 6-5 for all investigated samples obtained by µSEC-ICP/HRMS.

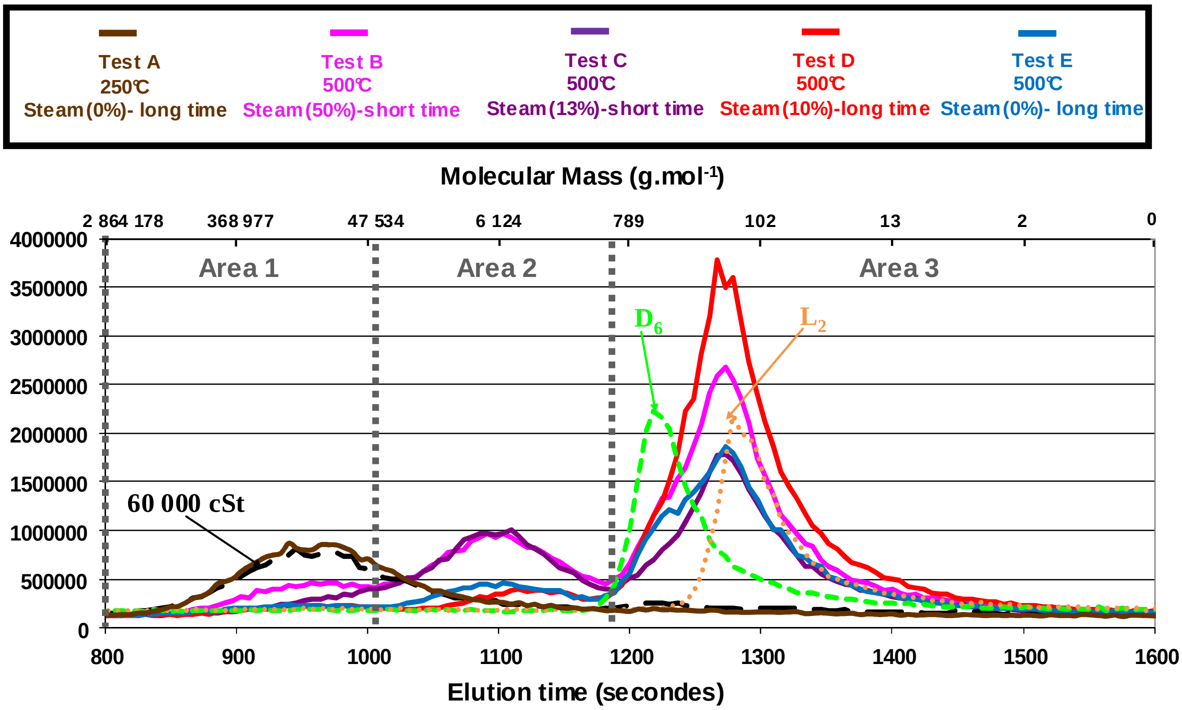


Figure 6-5. Typical µSEC-ICP/HRMS chromatograms obtained for the five degradation samples stored in liquid nitrogen at -195°C under conditions A, B, C, D and E. Three elution areas are defined for the quantification of silicon. The µSEC-ICP/HRMS of the PDMS 60,000 cSt, D_6 and L_2 standards are also overlaid for a comparison of the elution profile. A molecular mass range is also indicated for a better visualization of the results

6.3.5 PDMS degradation sample under conditions A at 250°C

For the PDMS degradation study performed at 250°C in the presence of hydrocarbons (Test A), the µSEC-ICP/HRMS chromatogram perfectly matched with the chromatogram of PDMS 60,000 cSt initially present (Figure 6-5). This result showed that the analytes obtained had a similar medium molecular mass around 115 10^3 $g.mol^{-1}$ as for the initial PDMS 60,000 cSt. This result was confirmed by the quantification approach by µSEC-ICP/HRMS which indicated that more than 94% of the silicon concentration was recovered from the elution area 1 and 2 similarly to the initial trend obtained for PDMS without degradation (Figure 6-6 and Table 6-5). As mentioned by other studies [9, 10, 13] that showed that PDMS does not begin to degrade under inert gas below 300°C, the presence of hydrocarbons similarly to refining processes operated at 250°C does not influence the PDMS degradation at low temperature. Problems caused by silicon on catalyst operating at 250°C in the presence of hydrocarbons in refining process cannot originate from the thermal degradation of PDMS. However, the presence of steam at this temperature under long residence time can have an influence on PDMS degradation and therefore in the poisoning of catalyst.

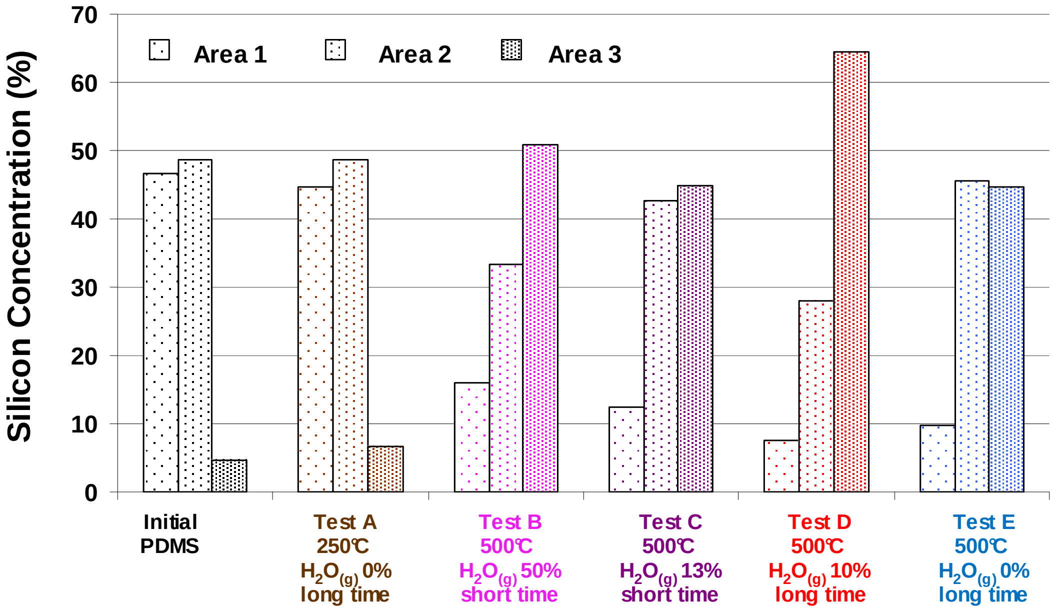


Figure 6-6. Comparison of silicon concentration in percentage for the three areas previously defined for all samples analyzed by µSEC-ICP/HRMS. All silicon concentration values are indicated in details in the Table 6-5

6.3.6 PDMS degradation samples at 500°C: Tests B, C, D and E

Under thermal cracking at 500°C and in the presence of hydrocarbons, PDMS degrades and forms compounds with different molecular masses. The different silicon compounds were eluted in three different areas with very different percentages of silicon depending on the residence time and the steam content. All µSEC-ICP/HRMS chromatograms obtained for the degradation samples under thermal cracking of hydrocarbons are presented in Figure 6-5. The silicon concentration are indicated in details in the Table 6-5 and displayed in percentage in Figure 6-6.

6.3.6.1 Degradation at 500°C with short residence times: Tests B and C

Two different percentages of steam for test B (13%) and C (50%) were applied under short residence time during the thermal cracking of hydrocarbons. For the test B (53%), a peak was present in the area 1 (Figure 6-5). This peak has a medium molecular mass of 112 10^3 g.mol^{-1}. This elution area falls within the initial elution area of PDMS 60,000 cSt (Figure 6-5). For the test C (13%), the elution peak has a medium molecular mass of and 90 10^3 g.mol^{-1}, also related to the initial PDMS elution area. Before the thermal degradation of the polymer, silicon concentration through PDMS represents around 46% of the total silicon concentration in area 1 (Figure 6-6 and Table 6-5). After the thermal cracking conditions at 500°C, around 16 and 12% of the silicon concentrations are present in the area 1, respectively for tests B

(50% of steam) and C (13% of steam). When using a high content of steam (50%), the initial PDMS is less degraded and the residual medium molecular mass of PDMS is more important. (Figure 6-5). These values confirm that PDMS was not completely degraded at 500°C under theses operating conditions (Figure 6-6 and Table 6-5).

Under B and C conditions, a second distribution clearly appeared for these tests in area 2 (Figure 6-5). The second distribution both observed for these two tests matched the intermediate polymers elution area with medium molecular masses of 6.5 10^3 g.mol^{-1} (Figure 6-5). The silicon concentration is more important in area 2 for the test C ($H_2O_{(g)}$ 13%) than for the test B ($H_2O_{(g)}$ 50%) and indicated that intermediate polymers are less degraded with a low percentage of steam. The presence of steam seems to promote the degradation of intermediate polymers. For these degradation samples (test B and C), the distribution is similar and can suggest the formation of the same linear PDMS with smaller units than initial PDMS or cyclic siloxanes with high degree of polymerization. Cyclic oligomers (D_n>D_{23}) of intermediate masses could be produced after a condensation of linear PDMS end blocked with OH group previously formed by initial PDMS hydrolysis [12].

A last distribution of silicon compounds is eluted in the area 3. According to the overlay of D_6 and L_2 µSEC-ICP/HRMS chromatograms, these silicon compounds would display a molecular weight below 500 g.mol^{-1}. Using the mass calibration curve, this distribution has a medium molecular mass of 177 g.mol^{-1}. Low molecular weight silicon compounds are more concentrated with 50% of steam content and are probably formed by the hydrolysis of intermediate polymers. A percentage of 84 and 88% of the total silicon concentration respectively for the test B and for the test C are recovered from area 2 and area 3 (Table 6-5 and Figure 6-6). These results confirm that at 500°C, when using a residence time and steam level similar to the steam cracking process, the majority of silicon species obtained appears to yield intermediate polymers and more specifically low molecular weight silicon compounds.

6.3.6.2 Degradation samples at 500°C with long residence time: Tests D and E

The degradation samples obtained with long residence times, demonstrated that the initial PDMS appeared to be totally degraded for tests D and E conditions respectively, either in the presence or absence of steam (Figure 6-5). The concentration obtained showed that less than 10% of the total silicon content is now recovered in area 1 after the degradation at 500°C whereas this can rise up to 45% for the initial PDMS 60,000 cSt. This result would confirm that PDMS degradation is more drastic during the evaluated visbreaking or coking conditions with long residence time (test D) than during the evaluated steam cracking conditions with short residence time at 500°C (test C). This result was in total agreement with the literature and confirmed that the PDMS degradation increases with increasing temperature conditions [10]. After this first step, possible reactions of hydrolysis and condensation could occur, especially when dealing with intermediate polymers. In the elution area 2, the previous distribution of intermediate polymers (tests B and C) is also present for the tests D and E. Medium molecular masses have been estimated to be at 4.5 and 7.5 10^3 g.mol^{-1} respectively for the test D and for the test E (Figure 6-5). According to their lower molecular mass, intermediate polymers produced under the test D conditions (long residence time and steam content) had smaller degrees of polymerization than intermediate polymers with all other conditions. The comparison of the tests D and E in terms of steam content confirms the previous trends observed for the short residence time tests B and C. The presence of steam increases the degradation of intermediate polymers, probably by hydrolysis mechanisms. Thus, the formation of low molecular weight silicon compounds is greater in the presence of steam (Figure 6-6).

These results are in full agreement with previous studies concerning thermal degradation of PDMS. They have reported that PDMS is degraded under inert gas at 500°C and formed low molecular silicon compounds. Cyclic siloxanes and trace of linear siloxanes were mainly produced [8-11] but no information about the PDMS degradation products under refining conditions was available. In this paper, PDMS was degraded at 500°C under evaluated thermal cracking of hydrocarbons such as visbreaking or coking and steam cracking on a pilot plant and characterized using µSEC-ICP/HRMS. For evaluated steam cracking conditions at 500°C (steam and short residence time), the initial PDMS was not completely degraded but silicon mainly appeared through intermediate polymers and LMW silicon species. Under evaluated visbreaking or coking conditions (long residence time), the initial PDMS is completely degraded. For all degradation tests at 500°C, the percentage of steam and the residence time have a great influence on the PDMS degradation to form LMW silicon compounds.

6.4 Conclusions

In order to improve our understanding of silicon speciation in the oil and gas industry, the production of representative samples of PDMS degradation under thermal cracking is necessary. Specific and sensitive analytical tools were applied to identify and quantify silicon compounds involved in catalyst poisoning.

In this paper, a pilot plant was especially adapted and designed for this work and used to produce representative samples of the degradation of antifoaming (PDMS) at 500°C under thermal cracking of hydrocarbons. Different percentages of steam were applied under short and long residence time to study the influence of these parameters on the PDMS degradation products. These samples were analyzed by µSEC-ICP/HRMS after a storage in the refrigerator at 4°C and in liquid nitrogen at -195°C to control the evolution of silicon species. This complete approach allowed the determination and the quantification of the different degradation products, especially high molecular weight molecules.

For low temperature process used in the oil and gas industry around 250°C, PDMS was not degraded in the presence of hydrocarbons. Silicon poisoning observed in catalyst at low temperature is not therefore likely to be due to the thermal degradation of PDMS. Under thermal cracking at 500°C in the presence of hydrocarbons, PDMS degraded and formed intermediate polymers of low molecular weight compounds with a small amount of residual PDMS ranged between 8 and 16% of the total silicon content following the different operating conditions. Under evaluated steam cracking conditions at 500°C, with short residence times, PDMS was not completely degraded and silicon concentration ranging from 12 to 16% was present through residual PDMS. Other resulting silicon species also appeared to belong to intermediate polymers and low molecular weight compounds. For evaluated visbreaking or coking conditions and with long residence time, the initial PDMS was totally degraded. Low and intermediate weight silicon compounds were the major degradation products. The percentage of steam has a great influence on the degradation of intermediate polymers probably by hydrolysis, to produce low molecular weight species mainly as cyclic siloxanes (D_n). To our knowledge, this is the first work reporting the homemade production of PDMS thermal degradation in representative petroleum products using a pilot plant coupled to the characterization of the samples. These results will improve the understanding of PDMS degradation under thermal cracking processes such as visbreaking, coking or steam cracking. The repartition of silicon between PDMS, intermediate polymers and low molecular weight compounds could explain the distribution of silicon amount in the different cuts of petroleum products and probably the poisoning effect on hydrotreatment catalyst. For a complete identification of low molecular weight compounds and especially new unknown silicon molecules potentially coming from the reactivity with hydrocarbons, a multi-analytical approach was developed and will be applied. These experiments are currently carried out in our laboratories and will be the subject of further works.

Chapitre 7. Molecular characterization of PDMS degradation samples produced under thermal cracking of hydrocarbons

7.1 Characterization of silicon species issued from PDMS degradation under thermal cracking of hydrocarbons: Part 1-Gas samples analysis by gas chromatography-time of flight mass spectrometry

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7.1.1 Abstract

Silicon species are becoming emergent contaminants in the oil and gas industry due to their severe poisoning effect on the hydrotreatment (HDT) catalysts. Using an experimental pilot plant, fresh and representative samples of PDMS degradation under thermal cracking of hydrocarbons were produced. To follow the evolution of silicon species, the gas fraction was immediately analyzed by GC/TOFMS after the production and also after four months of storage at 4°C. Cyclic siloxanes (D_n) as the major products of PDMS thermal degradation were characterized in the gas phase but these compounds are mainly present in the liquid fraction (Section 7.2). Five volatile silicon compounds belonging to the families of silanes, siloxanes and silanols were characterized and quantified in the thermal cracking samples depending on the operating conditions applied in degradation tests. Under coking or visbreaking conditions (long residence time, absence of steam), silanes and siloxanes were preferentially formed. Under evaluated steam cracking conditions (short residence time and presence of steam), trimethylsilanol (TMSOH) was mainly produced by the hydrolysis of PDMS. The formation of the linear siloxane (L_2) after several month of storage at 4°C by the self-condensation of TMSOH was also observed. The suspected poisoning effects of these molecules were discussed and could explain the deactivation of catalysts taking place in the refining of the light petroleum cuts. The new identified volatile silicon compounds could

affect the performance of the catalyst by the reaction of hydroxyl groups potentially present at the surface of the support with reactive silicon molecules, more specifically silanols.

7.1.2 Introduction

Silicon is probably the most widespread catalytic poison recovered in hydrotreatement feeds [4]. In petroleum products, silicon mainly originates from the use of antifoaming agents such as polydimethylsiloxanes (PDMS) to enhance the crude oil recovery from the reservoir and to avoid the formation of emulsions in the different processes such as coking, visbreaking, steamcracking or distillation [5, 30]. Despite of its rather good thermal stability, it degrades around 300°C [10, 13] and generates very different silicon degradation products which can react then with the hydrocarbon matrix. Such degradation processes of PDMS have been studied by Camino *et al.* [10, 11] in a pyrolyser apparatus under inert gas for 2 temperatures of operation 400°C and 800°C. Results showed that cyclic siloxanes (D_3-D_{13}) were the major degradation products with traces of linear siloxanes characterized by GC/MS in the liquid fraction. The gas phase was analyzed by Fourier tansform infra-red spectroscopy (FTIR). Except for the presence of CH_4, H_2O and CO_2, no information about the possible formation of volatile silicon species was available.

The literature on poisoning highlighted that silicon species can have a very different effect on the catalytic stage depending on the nature of the catalyst [32], on the experimental conditions [45] but more specifically on the chemical nature of the molecule [45]. Cyclic siloxanes (D_3-D_6), resulting from the thermal degradation of PDMS, were previously identified and quantified by gas chromatography coupled to mass spectrometry in single ion monitoring (GC/MS SIM) mode in naphtha and gasoline samples coming from a steam cracking process [18] but no study was yet reported on the possible poisoning effect of these molecules on HDT catalysts. Silanes, such as TrMS (trimethylsilane) and TMS (tetramethylsilane), were suspected to act as poisons for HDT catalyst stage [57]. Other silanes (SiH_4 [49], CH_3SiH [52], Et_3SiH [45, 46]) were clearly identified as catalyst poison during hydrogenation or dehydrogenation reactions. On the contrary, an increase of the selectivity of a Ni/Al_2O_3 catalyst was observed with $(CH_3)_2Si_2$ [49]. Among siloxane compounds, hexamethyldisiloxane (L_2) was defined to be the most severe poison for Pd or Pt catalysts when used for the oxidation of volatile organic compounds (VOC) in a biogas plant [64-67]. To progress on the understanding of silicon poisoning, the chemical nature of silicon species and their relative amount in the different petroleum cuts need to be investigated.

Due to the instability and the reactivity of several silicon compounds [84], the chemical nature of silicon species affecting the catalytic processes can be rather unstable and be modified prior to the speciation analysis achieved in the lab during the storage of the samples. Therefore, this could induce that the previous results reported on silicon speciation in naphtha and gasolines samples were not totally representative of the true silicon species initially present during the catalytic process [18, 279]. It is most likely that identified silicon species, after several weeks or months from the initial sampling, could be different from that of the initial silicon molecules possibly affecting the catalytic processes.

To understand the PDMS degradation products under thermal cracking of hydrocarbons and to characterize these silicon species, fresh samples were produced using an experimental pilot plant and were either directly analyzed or carefully stored before further analysis to minimize the evolution of silicon species [286]. A first analytical approach of the silicon species generated under these conditions have been performed and showed that, when using liquid separation by µSEC-ICP/HRMS, very different silicon compounds occurred over a wide range of molecular masses [286]. For a complete characterization of silicon molecules, the effluents must be analyzed by a multi-technical approach previously developed and using GC/MS in full scan mode and in SIM mode [18] and high resolution mass spectrometry (FT/MS) [279].

In this paper, we present the results obtained on the gas fraction characterization of the PDMS degradation studies. Indeed, the aim of this study is to highlight the volatile silicon compounds, which could affect the performance of HDT catalysts mainly on light petroleum cuts (C_1-C_4 and C_5^+). At first, head space (HS) hyphenated to GC/MS was performed to characterize the possible impurities present in the initial PDMS to secure that all characterized silicon compounds would really originate from the thermal degradation. Then, the gas fractions of the five degradation studies previously produced were analyzed by GC/TOFMS using a cryogenic nitrogen (N_2) valve. The formation of identified and quantified volatile silicon compounds were studied with respect to main critical steps of the process along the different operating conditions focused on the residence time and the steam content. The possible poisoning effect of these volatile silicon molecules were also discussed according to the previous catalytic tests reported in the literature.

7.1.3 Materials and Methods

7.1.3.1 Silicon standards and solutions

Four volatile silicon compounds were used as reference molecules for this study. These were chosen among a complete mixture used for the speciation of silicon in previous studies [18, 279]. Tetramethylsilane (TMS), trimethylsilanol (TMSOH), pentamethyldisiloxane (A) and hexamethyldisiloxane (L_2) were purchased from Sigma-Aldrich (Lyon, France). Acetone of LV-GC grade, especially for trace analysis, was obtained from Biosolve Chemicals (Valkenswaard, Netherlands). A mixture of these compounds at 0.5% in mass in acetone was prepared and different dilutions were achieved to evaluate the detection limits (LOD_s) and the linearity of the GC/TOFMS method. The storage and the complete analytical procedure to avoid silicon contamination were previously defined in Chainet *et al.* [18, 279].

7.1.3.2 Samples and analytical strategy

The degradation samples of PDMS under thermal cracking of hydrocarbons (heptane and xylene) were produced using a modified pilot plant [286]. All operating conditions are presented in Table 7-1. These conditions allowed to determine the influence of the temperature, the residence time and the steam content on the PDMS degradation products. They have been previously discussed in details in Chainet *et al.* [286]. To simulate a low temperature process in the oil and gas industry and to study the stability of PDMS, the test A was achieved at 250°C. Four tests were performed under thermal cracking of hydrocarbons at 500°C. This temperature was considered to be the reference temperature for the majority of the thermal cracking processes such as coking or visbreaking [36]. For a steam cracking process, the temperature is normally set at 800°C but in our case it was impossible to obtain this temperature without the formation of coke [286]. Due to the design of the pilot plant and the safety conditions needed, the evaluation of the steam cracking process was achieved at 500°C with short residence times and steam added with different percentages (test B and C) [286]. For the thermal cracking processes such as coking and visbreaking, a long residence time was applied with the adding of steam (test D) or not (test E) [286].

Table 7-1. Operating conditions of the process for all produced samples (Adapted from [286])

Tests	Temperature (°C)	Residence time (s)	Steam (%m)
A	250	long (5.50 s)	0%
B	500	short (0.64 s)	50%
C	500	short (0.49 s)	13%
D	500	long (3.48 s)	10%
E	500	long (3.50 s)	0%

Figure 7-1 presents the flow chart of the operation, sample collection and storage and analytical conditions. Using a condenser, the vapour of the degradation products of PDMS were cooled and condensed to obtain a gas fraction and a liquid fraction. The gas fraction collected with Tedlar bags of 1L with a polypropylene valve (Interchim, Montluçon, France). This fraction was immediately analyzed by GC/TOFMS using a N_2 cryogenic valve and then stored at 4°C in a refrigerator (Figure 7-1). Currently, no specific recommendations for silicon speciation were applied concerning the time and the conditions of storage of real samples coming from a refinery. To study the possible evolution of silicon compounds, the gas samples were qualitatively re-analyzed after four months storage of Tedlar bags at 4°C in the refrigerator.

The liquid fraction was analyzed by µSEC-ICP/HRMS for the characterization of high molecular weight silicon compounds [286]. For the characterization of low molecular silicon compounds in the liquid fraction, which are known to directly affect the performance of catalyst, several studies using GC/MS and FT-ICR/MS were also performed in our lab and will be the subject of the part 2 of this work (Figure 7-1) (section 7.2).

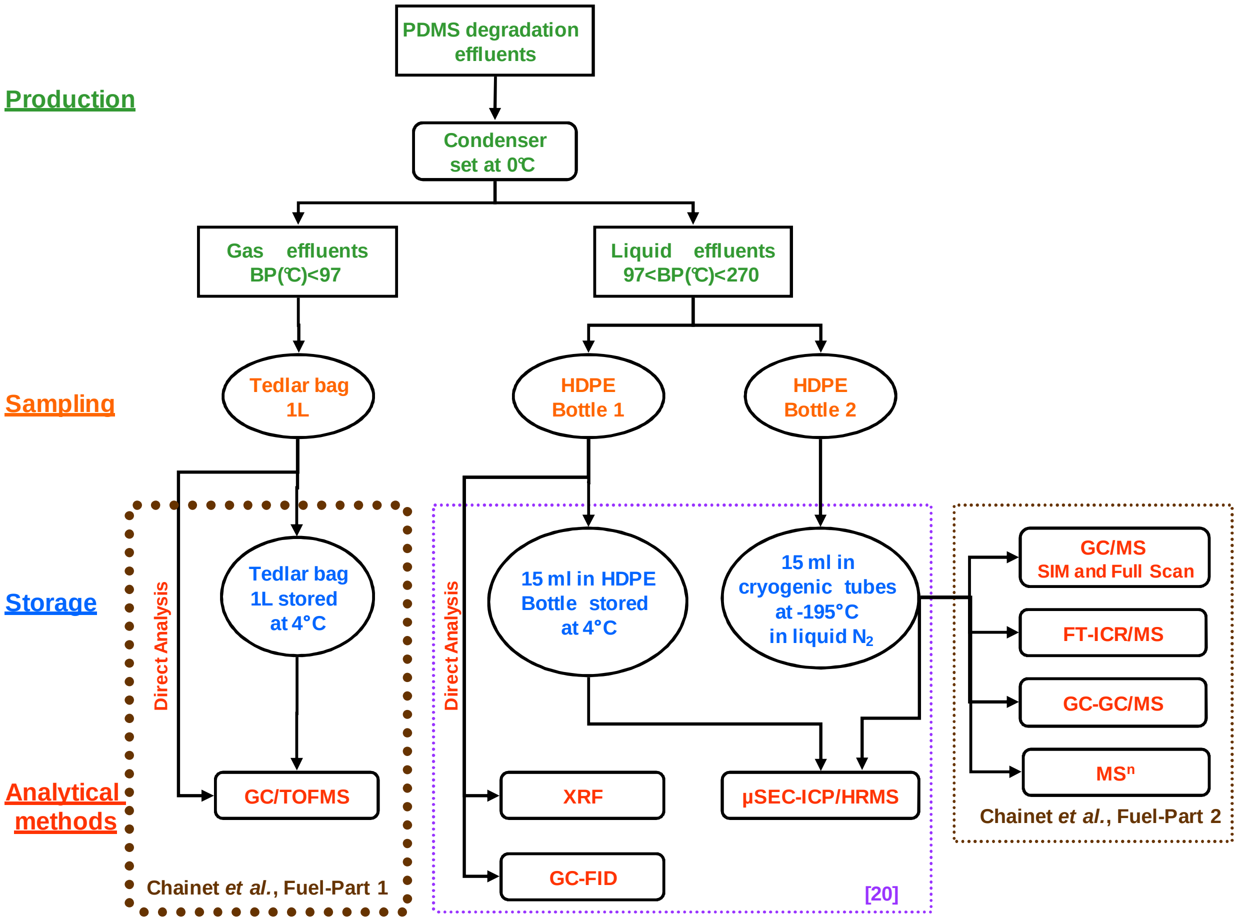


Figure 7-1. Flow chart of the analytical strategy for the effluent characterization (Adapted from [286])

7.1.3.3 Apparatus

7.1.3.3.1 HS-GC/MS

To be sure that no volatile silicon compounds were initially present in the PDMS 60,000 cSt, the polymer was analyzed by a head space (HS) system (HS Agilent G1888, Agilent technologies, Massy, France) hyphenated to a GC/MS. The GC/MS system was a gas chromatograph Agilent 6890 (Agilent technologies, Massy, France) coupled to a mass spectrometer (HP5973N, Agilent technologies, Massy, France). A sample of 1 g of pure PDMS was heated at 100°C during 30 minutes in a 10 ml airtight closed bottle with a septum made of PTFE/silicon (Agilent technologies, Massy, France). A volume of 1 ml with a split ratio of 10:1 of the gas phase was then analyzed by GC/MS using the following analytical conditions. The separation was achieved on a DB624 column (30mx0.32mm i.d., 1.80µm film thickness) from J&W Scientific (Folsom, CA, USA). An injection temperature of 240°C was used with helium as a carrier gas at 2.5 ml.min^{-1} constant flow rate. The oven temperature was programmed from 40°C (7 min) to 240°C (10 min) at 20°C.min^{-1}. The total run time was 27 min. The mass spectrometer equipped with electron impact ionization source set at 70 eV and 230 °C was operated in full scan mode for a mass range from m/z 25 to m/z 300. The mass spectra were compared against the NIST database (National Institute of Standards and Technology, Gaithersburg, MD, USA version 2005).

7.1.3.3.2 GC/TOFMS

All gas samples were analyzed using the AccuTOF GC (JEOL, Tokyo, Japan). This hyphenated system was equipped with a gas chromatograph Agilent 7890 (Agilent technologies, Massy, France) coupled to a time of flight mass spectrometer (TOFMS) (JEOL, Tokyo, Japan). The separation was achieved with a DB-5 MS UI column (30mx0.25mm i.d., 0.50µm film thickness) from J&W Scientific (Folsom, CA, USA). A volume of 500 µl of gas was injected with a split ratio 1:10 through a BTO septum (Restek, Lisses, France). An injection temperature of 200°C was used with helium as a carrier gas at 0.9 ml.min^{-1} constant flow rate. For the determination of volatile silicon compounds, the oven temperature was programmed from -60°C (10 min) to 280°C (2min) at 5°C.min^{-1}. The total run time was 80 min. The mass spectrometer equipped with electron impact ionization source set at 70 eV and 200 °C was operated for a mass range starting from m/z 10 to m/z 300. The mass spectra were compared to the Wiley Registry 9th Edition (John Wiley & Sons, Inc., New York, USA, 2010) / NIST 2011 Mass Spectral Library (National Institute of Standards and Technology, Gaithersburg, MD, USA version 2011).

7.1.4 Results and discussion

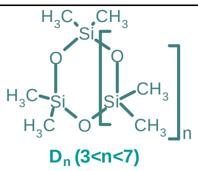
PDMS was first analyzed by HS-GC/MS to determine the possible presence of silicon impurities and to be sure that volatile silicon characterized by GC/TOFMS would only originate from the thermal degradation of PDMS under thermal cracking of hydrocarbons. Previous works by µSEC-ICP/HRMS on the liquid fraction of the samples have shown that PDMS degraded at 500°C and will form intermediate polymers and more specifically low molecular weight silicon compounds [286]. After validation of the GC/TOFMS method, all the gas fractions of the five PDMS degradation samples were analyzed to determine and quantify volatile silicon compounds. These compounds will be present in the light petroleum cuts and poison HDT catalysts.

7.1.4.1 Characterization of the PDMS gas phase by HS-GC/MS

An air blank was always performed before and after the analysis of the sample by HS-GC/MS. It demonstrated that no contamination by silicon compounds would occur. These precautions were taken since previous studies have shown that several contaminations could take place during silicon analysis, especially by cyclic siloxanes (D_n). These compounds can come from contamination by the GC inlet, the GC column bleeding or especially from the cap of the vial [14].

Table 7-2 presents the results of the analysis of the PDMS gas phase injected after heating pure PDMS at 100°C during 30 minutes by HS-GC/MS. In the PDMS sample gas phase, we have only detected cyclic siloxanes ranging from D_3 to D_7. They were characterized by their mass spectrum with some traces of hydrocarbons. D_4 (octamethylcyclotetrasiloxane) was the most important compound characterized and present in the gas phase after heating the PDMS at 100°C during 30 minutes. D_4 cyclic siloxane was used for the synthesis of the PDMS and it was not surprising to detect this compound with other D_n in the gas phase of the initial formulation of PDMS [91]. Except for this molecule, the relative amount of cyclic siloxane decrease with the increase of their polymerization degree [14, 18]. These molecules were clearly defined as the major degradation products of PDMS in the literature. However it was previously stated that PDMS should not begin to degrade under 300°C [10, 13]. Indeed, Camino *et al.* [10] have demonstrated using thermogravimetric analysis that the mass of PDMS did not decrease before 300°C. However, some impurities of cyclic siloxanes (D_3-D_7) and especially D_4 were characterized in small quantities in the gas phase of the initial PDMS. According to the literature, no poisoning effects have been evidenced for these molecules. Also, no other volatile silicon compounds were detected in the gas phase by HS-GC/MS. This result allowed to confirm that the presence of potential silicon molecules after the thermal cracking would only originate from the PDMS degradation. The search for these volatile silicon compounds produced after the PDMS degradation samples under thermal cracking of hydrocarbons will be achieved by GC/TOFMS after the validation of the method.

Table 7-2. Results of the HS-GC/MS analysis of the gas phase when heating the pure PDMS 60,000 cSt at 100°C during 30 minutes

Molecules	Retention time (min)	Relative intensity (%)	Chemical formula
D_3	10.34	33.69	
D_4	12.45	100.00	
D_5	13.94	13.89	
D_6	15.28	1.53	
D_7	16.58	0.26	

The repetition pattern C_2H_6OSi is indicated as the abbreviation D for silicon compound relative to the number of oxygen attached to a silicon atom.

7.1.4.2 Validation of the GC/TOFMS method

In order to characterize the gas fraction of the samples, the analytical performance of the GC/TOFMS method was evaluated using the four volatile silicon compounds previously described. Table 7-3 presents the different results obtained for the validation of the method. Detection and quantification limits are respectively calculated considering a signal to noise ratio of 3 and 10 in acetone spiked with a solution at 50 µg.kg^{-1} of silicon compounds. The characterization of silicon compounds in gas samples was based on retention time comparison with the standard mixture of silicon standards and on their relative mass spectrum. Quantification is based on the measurement of one specific ion per molecule extracted from the TIC (total current ion) chromatogram. The specific ion selected for each silicon compound was achieved because it was the most abundant (Table 7-3). An internal standard (M_4Q) was used to take into account the day by day MS variations but the MS response appeared to be very stable (less than 5% variation on the peak area). The calibration curves were linear up to 1000 µg.kg^{-1} with correlation coefficients more than 0.991. Quantification limits ranging from 2.3 to 14.7 µg.kg^{-1} are obtained in acetone. After this validation step, the analytical method was applied to the samples in order to identify and quantify silicon compounds which would be candidate poisons for HDT catalysts.

Table 7-3. Validation data for the GC/TOFMS method

Molecules	t_R (min)	Ion (quant.)	Linearity		LOD	LOQ
			Equation y=ax+b	R^2	µg.kg^{-1}	
Tetramethylsilane (TMS)	17.28	73	y=328352x-9893	0.993	4.4	14.7
Trimethylsilanol (TMSOH)	25.15	75	y=353421x-7500	0.991	0.7	2.3
Pentamethylsiloxane (A)	27.77	133	y=318641x-6510	0.995	1.9	6.3
Hexamethyldisiloxane (L_2)	29.74	147	y=546835x+8650	0.999	3.3	11.1
Internal standard (M_4Q)	47.33	281	--	--	0.1	0.4

7.1.4.3 *Speciation of volatile silicon compounds*

To avoid the possible evolution of silicon species, the gas fractions of the five PDMS degradation studies were immediately analyzed by the GC/TOFMS method after the production using the pilot plant. All silicon compounds characterized in the five samples with their relative concentration depending on the operating conditions are presented in Table 7-4. Cyclic siloxanes (D_n), silanes, trimethylsilanol (TMSOH) and linear siloxanes were present in these samples and could be potentially responsible of catalyst poisoning. The detected cyclic siloxanes (D_3-D_7) are mainly recovered in the liquid fraction of our samples at high concentration (Figure 7-3) and the relative quantification of these molecules is provided in the part 2 of this work (section 7.2).

Table 7-4. Concentration of identified volatile silicon species in all degradation samples directly analyzed by GC/TOFMS

M	t_R (min)	Test A	Test B	Test C	Test D	Test E
		Concentration (µg.kg^{-1})				
TrMS	12.83	n.d.	n.d.	n.d.	64	219
TMS	17.29	n.d.	n.q.	35	90	298
TMSOH	25.12	n.q.	84	63	555	261
A	27.73	n.d.	n.d.	n.d.	26	30
L_2	29.74	n.d.	n.d.	n.d.	n.q.	18
D_3	35.38	d.	d.	d.	d.	d.
D_4	41.42	d.	d.	d.	d.	d.
D_5	46.41	n.d.	d.	d.	d.	d.
D_6	51.35	n.d.	d.	d.	d.	d.
D_7	55.78	n.d.	d.	d.	d.	d.

n.d. not detected; n.q. not quantified; d. The D_n are detected but the relative quantification is provided in the part 2 of the paper focusing on the analysis of the liquid fraction (section 7.2).

To verify the conversion of the initial source of hydrocarbons, the GC/TOFMS analysis allowed the characterization of the thermally cracked products of the mixture of heptane and xylene. This mixture was converted in several hydrocarbons ranging from C_1 from C_{15} (Figure 7-2-a). A more detailed analysis of hydrocarbons by GC-FID per family was available in Chainet *et al.* [286]. These light hydrocarbons, especially olefins and aromatics can react with PDMS degradation products at 500°C to form new unknown silicon molecules. Among the five degradation tests (A, B, C, D and E), the test E was achieved at 500°C under evaluated conditions of coking or visbreaking with a long residence time and without steam. This test was chosen to be illustrated in Figure 7-2 because all silicon species highlighted in this work were characterized in this degradation test (Table 7-4). Figure 7-2 (b, c and d) shows the mass chromatograms of the five volatile silicon compounds identified by their retention time and their mass spectrum in the PDMS degradation test E. These results will be discussed following the different conditions of temperature (250 and 500°C), residence times and steam content applied in the degradation studies.

On the contrary to the SIM mode acquisition [18], the TOF/MS acquisition mode allowed to specifically search for other silicon compounds with their specific ions from the TIC chromatogram of each PDMS degradation gas sample. Other methylsilanols with a higher degree of polymerization, siloxanediols, dimethoxysilanes, silanes or siloxanes were searched but these molecules were not detected in the gas phase. The complete characterization of silicon compounds in the liquid fraction of the PDMS degradation samples including some of these silicon species is available in the part 2 of this work (Section 5.2).

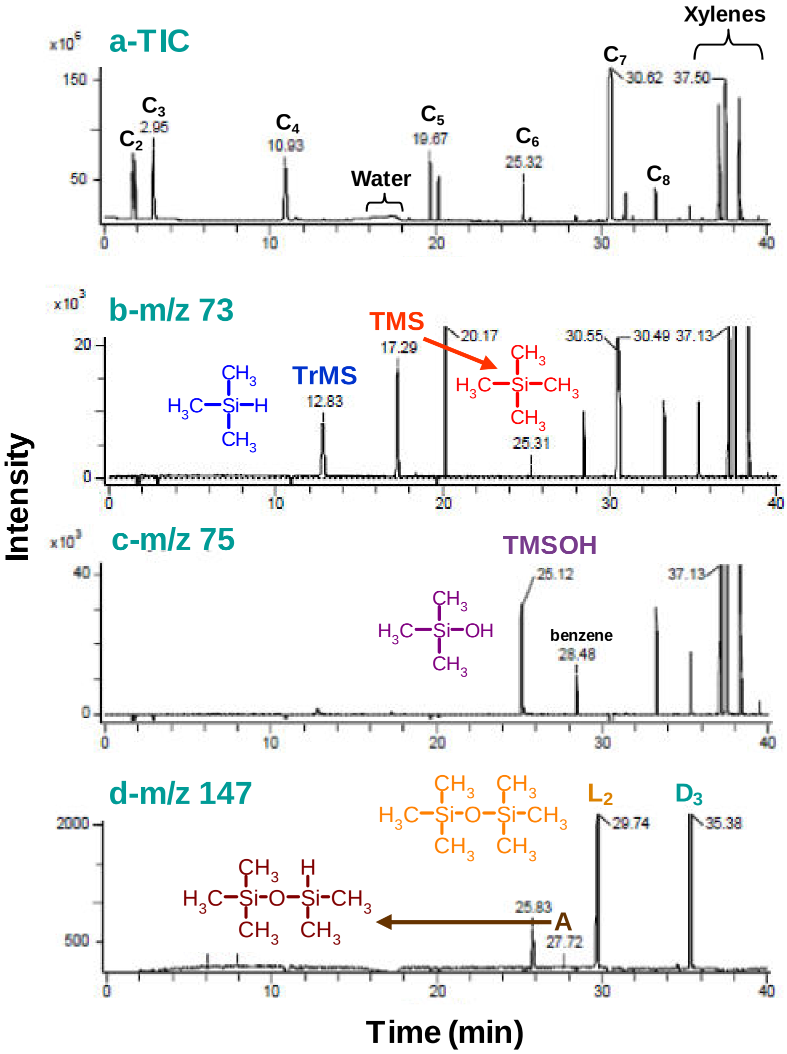


Figure 7-2. 40 minutes zoom of the GC/TOFMS TIC chromatogram obtained for the test E under evaluated cokefaction or visbreaking conditions (500°C, 0% of steam, long residence time) (a), Ion m/z 73 mass chromatogram of the test E (b), Ion m/z 75 mass chromatogram of the test E (c), Ion m/z 147 mass chromatogram of the test E (d). C_2-C_8: hydrocarbons, TrMS: trimethylsilane, TMS: tetramethylsilane, TMSOH: trimethylsilanol, A: pentamethylsiloxane, L_2: hexamethyldisiloxane, D_3: octamethylcyclotrisiloxane

7.1.4.3.1 PDMS degradation sample under conditions A at 250°C

This test was achieved to study the stability of the PDMS at 250°C because silicon seems to cause problems in processes used in the oil and gas industry at low temperature. Previous µ-SEC-ICP/HRMS analyses of the liquid fraction have demonstrated that PDMS does not degrade in the test A conditions [286]. The GC/TOFMS analysis of the gas fraction confirmed this result because no volatile silicon compounds were detected (Table 7-4). Figure 7-3 presents the comparison of three chromatograms obtained after the GC/TOFMS analysis of a blank of air (a), the test A (b) and the test E (c) in order to particularly emphasize the detection of cyclic siloxanes. In the test A conditions, only compounds such as D_3 and D_4 were detected (Figure 7-3b). These species are known to be the major products of the thermal degradation of PDMS, but above 300°C and under inert gas [11, 14, 18, 286]. As previously demonstrated in the section 7.1.4.1, cyclic siloxanes (D_n) were initially present as impurities in the gas phase of the initial PDMS but these molecules did not act as poison for HDT catalyst.

These series of molecules were also detected at trace levels in the analytical blanks of air by GC/TOFMS (Figure 7-3-a). The intensity of D_n in the blank of air is similar to the intensity measured for the test A (Figure 7-3). This small amount of cyclic siloxanes may come from the initial impurities analyzed by HS-GC/MS or from the thermal degradation of the inlet septum made of silicones [18] during the analysis. Indeed, the previous precautions taken previously with the Merlin injection system valve previously used in silicon speciation to avoid contaminations by D_n cannot be used for gas samples injection [18]. Except for TMSOH (S/N of 6 in one blank of air), no others compounds could be detected in the blanks performed between each GC/TOFMS analysis.

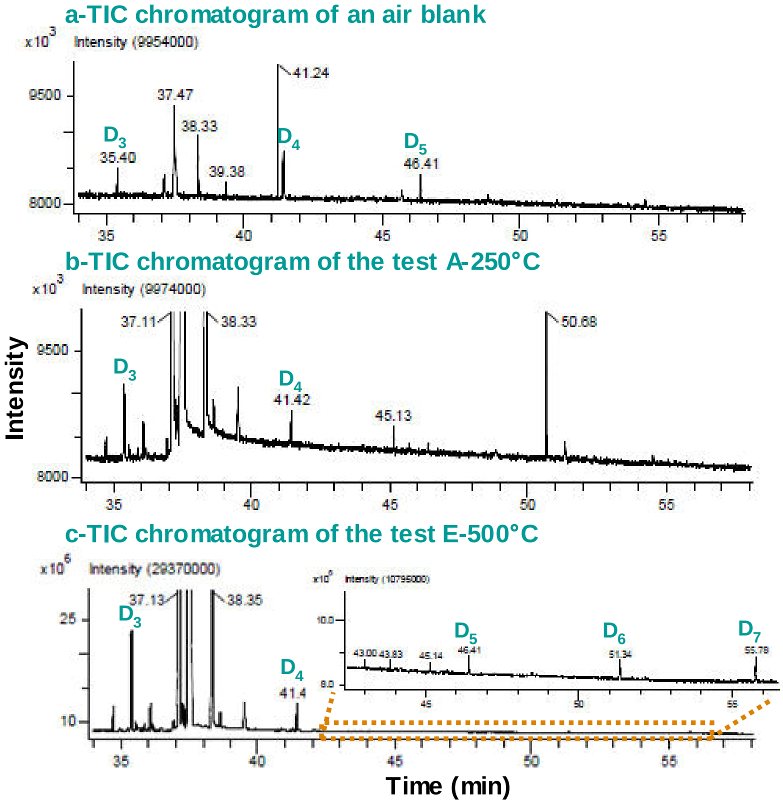


Figure 7-3. Zoom of the GC/TOFMS TIC chromatogram between 34 and 58 minutes obtained for an air blank (a), the test A (250°C, 0% of steam, long residence time) (b) and the test E under evaluated cokefaction or visbreaking conditions (500°C, 0% of steam, long residence time) (c) illustrating the detection of cyclic siloxanes (D_3-D_7)

7.1.4.3.2 PDMS degradation samples at 500°C: Tests B, C, D and E

In all other degradation tests performed at 500°C, cyclic siloxanes (D_3-D_7) are the major silicon degradation products. They were occurred and characterized at high concentrations but they are mainly present in the liquid fraction due to their lower boiling points (Figure 7-3-c) [11]. Even if cyclic siloxanes (D_n) were the most abundant PDMS degradation products characterized in the degradation samples and also in gasolines previously analyzed [18], no poisoning effect on catalyst was already demonstrated in the literature for these molecules. Therefore, other more reactive silicon molecules such as silanes, silanols or linear siloxanes could then affect the performance of HDT catalysts. The potential poisoning effects of these molecules will further discussed in the section 7.1.4.5.

7.1.4.3.2.1 Degradation at 500°C with short residence times: Tests B and C

During the short residence times experimental conditions, two different percentages of steam were used for the test B (50%) and for the test C (13%) under thermal cracking of hydrocarbons. In the B test conditions in the presence of a high steam content, no silanes were detected. When the steam content was decreases for the same residence time, the degradation conditions are more drastic and tetramethylsilane (TMS) was also quantified at 35 µg.kg^{-1} in the test C. In term of species identification, only trimethylsilanol (TMSOH) could be identified in the test B and in all degradation tests at 500°C (Figure 7-2-c and Table 7-4). The quantity of TMSOH decreases with the diminution of the steam content from the test B (84 µg.kg^{-1}) to the test C (63 µg.kg^{-1}). The formation of TMSOH is probably due to the hydrolysis of PDMS [306] but a comparison of the results for this compound between the test D and the test E is necessary to confirm its formation mechanism. Under short residence time, only tetramethylsilane and trimethylsilanol were formed but when increasing the residence time, more volatile silicon compounds will be produced.

7.1.4.3.2.2 Degradation samples at 500°C with long residence times: Tests D and E

The gas fractions GC/TOFMS analysis of the degradation tests D and E confirmed the previous observation by µSEC-ICP/HRMS [286]. The initial PDMS is totally degraded [286] and a great number of volatile silicon compounds were produced under long residence times (Table 7-4).

Trimethylsilane (TrMS) and tetramethylsilane (TMS) were respectively characterized and quantified in tests D and E (Figure 7-2-b and Table 7-4). Concentrations of 219 and 298 µg.kg^{-1} were respectively obtained for TrMS and TMS in the test E. Thus, silanes were preferentially formed for long residence time and especially without steam (test E) under evaluated cokefaction or visbreaking conditions (Table 4). The formation of silanes from the degradation of PDMS under thermal cracking of hydrocarbons is probably due to a radical mechanism initiated by the scission of the Si-CH_3 bond [10].

Concerning the occurrence of TMSOH, previously characterized under short residence times, its relative concentration is more important in the test D than in the test E. This would confirm that the formation of TMSOH is probably due to the hydrolysis of the CH_3 end group of PDMS [306]. The hydrolysis reaction which is taking place in the test E in the absence of steam can be explained by the natural occurrence of water in heptane and xylene (initial concentration<150 ppm in the mixture of heptane and xylene) initially used as source of hydrocarbons. Silanol was preferentially formed under thermal cracking of hydrocarbons for long residence times conditions and in the presence of steam.

When running the experiments under the evaluated coking or visbreaking conditions with a long residence time, compounds such as pentamethylsiloxane (A) and hexamethyldisiloxane (L_2) were detected in tests D and E conditions (Figure 7-2-d). The A molecule was quantified to be around 26 and 30 $\mu g.kg^{-1}$ in the test D and E respectively. Hexamethyldisiloxane (L_2) was detected in the two tests but could only be quantified at 18.4 $\mu g.kg^{-1}$ in the test E with a long residence time and in the absence of steam (Table 7-4). These two linear siloxanes (A and L_2) were mainly produced during PDMS thermal degradation tests under the evaluated coking or visbreaking conditions (Table 7-4). Hexamethyldisiloxane was mainly formed by a depolymerization mechanism which consists in the formation of cyclic siloxanes (D_n) and also linear siloxanes (L_n) [10, 11, 13]. Pentamethylsiloxane (A) can be also obtained by the same mechanism followed by the cleavage of the $Si-CH_3$ to form a Si-H by a radical mechanism [10].

During PDMS thermal degradation at 500°C and under the evaluated coking or visbreaking conditions (long residence time), silanes (TrMS and TMS) and linear siloxanes (A and L_2) were produced at higher concentrations (Table 7-4). The concentration of TMSOH was only reported to be higher in the test D (10% of steam) compared to the test E conditions (0% of steam). This would confirm that the formation of trimethylsilanol is due to the hydrolysis of PDMS [306] (Table 7-2 and Table 7-4).

7.1.4.4 Evolution of silicon compounds

For the first time, five volatile silicon compounds potentially responsible of catalyst poisoning were characterized in gas petroleum samples. These five volatile silicon compounds are known to be very reactive, especially TMSOH, because silanols are generally unstable and tend to condense in acidic or alkaline environments to produce siloxanes [302]. The reactivity of these volatile silicon compounds to form other silicon species is crucial to obtain a representative silicon speciation. To determine if the silicon speciation changes during the storage, the gas samples were re-analyzed qualitatively by the same GC/TOFMS method.

The signal ratio respectively for L_2 and TMSOH obtained in the first analysis of gas samples were compared to the second analysis after four months of storage at 4°C. For the gas fraction of the test A produced at 250°C, this second GC/TOFMS analysis confirmed that no volatile silicon compounds were detected. In all degradation tests at 500°C, the amount of TMSOH tends to decrease and the quantity of L_2 drastically increases in all degradation samples at

500°C. The signal to noise ratio between L_2 and TMSOH increases by a factor 3 to 25 depending on the degradation test. This tendency clearly demonstrated the self-condensation of trimethylsilanol to form hexamethyldisiloxane as illustrated in Figure 7-4. This first result concerning the evolution of silicon compounds in gas petroleum samples is crucial for the understanding of catalyst poisoning. In fact, silicon speciation in real samples coming from refining processes was achieved after a period of storage. During this time period, the initially present silicon compounds are transformed before the analysis of samples and real silicon molecules potentially poison cannot be identified. The analysis of silicon compounds must be achieved quickly after the sampling to be representative of the silicon species that can poison catalysts.

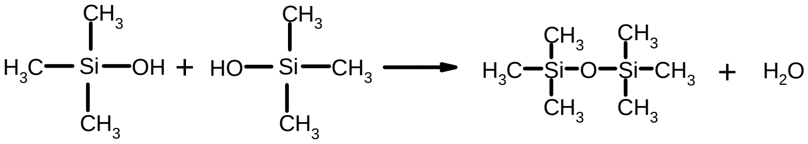


Figure 7-4. Formation of L_2 by a condensation reaction of TMSOH observed after four months of storage at 4°C

7.1.4.5 Potential impact on catalyst

The identification of these new silicon molecules coming from the thermal degradation of PDMS in the presence of hydrocarbons is very useful for the oil and gas industry. Silicon compounds such as cyclic siloxanes previously identified by GC/MS SIM are mainly recovered in the naphtha and gasoline range (20°C<BP<200°C) [4, 18] with a possible small amount of D_3 and D_4 in lighter cuts. According to their boiling points (7°C<BP<100°C), the identified volatile silicon compounds in this work can be present in light petroleum cuts (-100°C<C_1-C_4<20°C) and in naphtha and gasolines (20°C<C_5^+<200°C) where severe problems of silicon poisoning were suspected [43, 307]. Table 7-5 summarizes the different operating conditions for the formation of the volatile PDMS degradation products characterized in this work. The studies already reported on catalytic tests with silicon standard molecules (silanes, silanols and siloxanes) are also detailed and further discussed in the next section by family (Table 7-5).

Table 7-5. Operating conditions for the formation of volatile silicon species and their relative impact on catalysts

Molecules (BP °C)	Conditions of formation at 500°C	Previous works on silicon poisoning per family	Refs.
Silanes TrMS (7°C)	Evaluated coking or visbreaking conditions: -Long residence time -Quantity more important without steam -Formation by Si-CH_3 scission of PDMS [10]	-TrMS and TMS suspected as poison on Pd catalyst for cyclohexene deshydrogenation -Triethylsilane, Et_3SiH, characterized as severe poison on Pd and Pt catalysts for cyclohexene deshydrogenation	[57] [45, 46]
TMS (27°C)		-Methylsilane, CH_3SiH, defined as poison on Ni catalyst at 0°C -Hexamethyldisilane, $(CH_3)_2Si_2$, increased the selectivity for the production of benzene -Silane, SiH_4, suppressed the activity on Ni/Al_2O_3 catalyst for the deshydrogenation of cyclohexane	[52] [49]
Silanols	-Hydrolysis of PDMS -Favoured for long residence time	-Poisoning by adsorbed silicon species with $\equiv Si(OH)$, $=Si(OH)_2$, $\equiv SiCH_3$, $=SiOHCH_3$ and $=Si(CH_3)_2$ groups characterized by NMR on spent hydrotreatement surface catalysts for coker feeds	[50]
TMSOH (98°C)		-Reaction of methylsilanols such as TMSOH with a hydrated silica surface caused the adsorption of the silicon species	[308]
Siloxanes A (86°C)	Evaluated coking or visbreaking conditions: -Long residence time -Quantity more important without steam -Formation by a depolymerization mechanism [10]	Never tested for catalyst poisoning	--
L_2 (100°C)		L_2 defined as a severe poison on Pt and Pd catalysts for VOC oxidation in biogas	[64-67]

The state of the art on silicon poisoning reported that silicon compounds can have very different effects on the activity of a catalyst. Nuzzo *et al.* [49] have demonstrated that two silanes have different effects on Ni/Al_2O_3 catalyst for the dehydrogenation of cyclohexane. In the first case, hexamethyldisiloxane ($(CH_3)_2Si_2$) increased the selectivity of the catalyst for the production of benzene. In the second case, silane (SiH_4) suppresses the hydrogenolysis activity [49] (Table 7-5). Therefore, without knowing the exact chemical nature of silicon compounds in petroleum products, it was difficult to achieve representative catalytic tests. In this work, the determination of the chemical nature of various volatile and reactive silicon compounds was fully performed. For compounds such as TrMS and TMS, previous catalytic tests have been performed but no study could clearly demonstrate there poisoning effect on the catalysts. Other silanes also display a severe poising effect on Pd, Ni or Pt catalyst generally used during HDT (Table 7-5). As indicated in Table 7-4, trimethylsilanol is always produced during PDMS degradation under thermal cracking of hydrocarbons. Under severe refining conditions (high temperature, steam), the surface of the catalyst (alumina [56] or silica [308]) can be transformed and the amount of hydroxyl groups could increase. This phenomenon is illustrated in Figure 7-4. TMSOH occurring in petroleum products (Figure 7-5, scheme a) reacts with the hydroxyl groups of the surface through a condensation reaction to form an adsorbed silicon species at the surface (Fig. 4, scheme b). Kellberg *et al.* [50] have clearly demonstrated that the life time of HDT catalysts was drastically reduced due to the presence of analogous silica gels with different chemical structures at the surface of the catalyst (Table 7-5 and Figure 7-5).

Hexamethyldisiloxane (L_2) was directly produced by the PDMS degradation and also by the condensation of trimethylsilanol in all degradation samples after a period of storage. This siloxane, known to severely affect the performance of $Pt/\gamma-Al_2O_3$ catalyst used in the biogas industry (Table 7-5), was mainly characterized under evaluated coking or visbreaking conditions. The highlight of these new volatile silicon compounds during PDMS thermal degradation in the presence of hydrocarbons could potentially explained the poisoning of light petroleum cuts observed in the refinery.

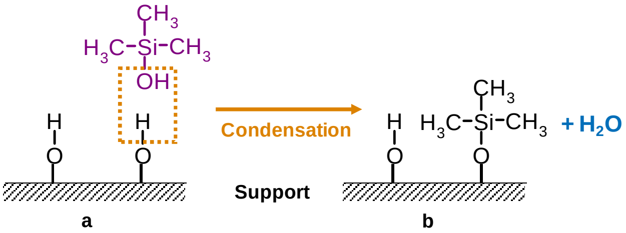


Figure 7-5. Proposed reaction of condensation between the hydroxyl groups of the catalytic surface and TMSOH [308]

7.1.5 Conclusions

In this study, representative samples of PDMS degradation under thermal cracking of hydrocarbons were produced on an experimental pilot plant. The gas fraction of the five degradation tests were then analyzed by GC/TOFMS to characterize volatile silicon compounds potentially responsible of the poisoning of light petroleum cuts.

At 250°C, except cyclic siloxanes (D_n) initially present in the initial PDMS gas phase, no other volatile silicon compounds were characterized and confirmed that PDMS did not degrade at this temperature. At 500°C, cyclic siloxanes (D_3-D_7) were also characterized at high concentrations and appeared as the major PDMS thermal degradation. They are mainly recovered in the liquid fraction but no poisoning effect was previously demonstrated. Their occurrence will be discussed in the part 2 of this work.

Under coking or visbreaking conditions at 500°C, PDMS degraded and formed different volatile silicon compounds at lower concentrations such as silanes, linear siloxanes and silanol which can act as severe poisons. The residence time and the presence of steam considerably influence the nature of PDMS degradation products. Under a long residence time without steam (coking or visbreaking conditions), silanes and linear siloxanes were preferentially formed. Trimethylsilanol was produced in all degradation tests by the hydrolysis of PDMS. Under steam cracking conditions at 500°C with a high content of steam, silanes and siloxanes were not detected. However, after several months of storage at 4°C, the instability of trimethylsilanol (TMSOH) caused its self-condensation to form hexamethyldisiloxane (L_2) in all degradation samples. This siloxane is well-known for its action as a severe poison for catalysts. The condensation of TMSOH in gas samples could be also observed at the surface of the catalytic support to form adsorbed silicon species that can severely reduce the life cycle of the catalyst.

The evolution of silicon species in these samples must be integrated for silicon speciation and further investigated in liquid samples to bring several recommendations. This PDMS added as antifoaming in very different stages of the refining processes causes the formation of various and volatile silicon compounds which can be recovered from light petroleum cuts (C_1-C_4) and naphtha to others petroleum cuts through their relative boiling points. Further poisoning tests on HDT catalysts using these new silicon compounds must be performed to verify their effect on the catalytic activity. The complete characterization of silicon compounds in the liquid fraction including cyclic siloxanes was performed in our lab by a multi-technical approach and will be the subject of the second part of this work (section 7.2).

7.2 Characterization of silicon molecules issued from PDMS degradation under thermal cracking of hydrocarbons: Part 2-Liquid samples analysis by a multi-technical approach based on gas chromatography and mass spectrometry

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7.2.1 Abstract

Silicon speciation has recently gain interest in the oil and gas industry due to the impact of silicon species on hydrotreatment (HDT) catalysts. The determination of the chemical structure of silicon compounds appeared as essential to limit silicon poisoning and to improve the life time of the catalysts. To achieve a representative speciation of silicon in petroleum products, fresh samples of PDMS degradation under thermal cracking of hydrocarbons were produced using a pilot plant. The samples were carefully stored in a dewar containing liquid nitrogen (-195°C) to minimize the possible evolution of silicon species and to allow their analysis in representative conditions. A complete analytical approach based on gas chromatography (GC) and mass spectrometry techniques (MS) was developed and applied to the samples produced at 500°C. Moreover, to resolve coelutions observed by GC/TOFMS, GC-GC/TOFMS was successfully applied to obtain the mass spectrum of only one silicon compound. Combining the GC/MS mass spectrum giving access to the fragmentation of the compound and the raw formula and double bond equivalent (DBE) obtained by ESI-FT-ICR/MS, chemical structures were proposed. Almost silicon molecules were strengthened by MS^n.

Cyclic siloxanes (D_n) were confirmed as the major compounds of PDMS thermal degradation even in the presence of hydrocarbons with a relative amount generally around 95% or above. No significant differences on the formation of D_n were observed according to the different operating conditions under thermal cracking of hydrocarbons. For the first time, several other silicon compounds present at trace levels (<5% of the total area) were characterized. α,ω-dihydroxy polydimethylsiloxanes, methylhydroxy cyclic siloxanes, cyclic silanone or bis(cyclosiloxanyl)siloxane, α-hydroxy,ω-methyl polysiloxanes and sylene cyclic siloxanes

were preferentially formed in the presence of steam. Under evaluated coking or visbreaking conditions (long residence time without steam), other compounds were mainly characterized such as dimethoxy polysiloxanes, methyl(hydroperoxy) cyclic siloxanes, methyl(hydroxyethyl) cyclic siloxanes, linear polysiloxanes and methylpropyl cyclic siloxanes. However, cyclic silanones and sylene cyclic siloxanes were known to be very unstable but these chemical structures were the most plausible. Around one hundred silicon compounds were highlighted belonging to 10 different families. The same repetition pattern (C_2H_6OSi), initially present in the PDMS, was present in all silicon compounds characterized in this study. Molecules with a number of silicon atoms ranging from 1 to 40 silicon atoms clearly demonstrated the occurrence of silicon in all petroleum cuts through their chemical structures. In fact, silicon species can distillate from gas fractions to the heavy petroleum cuts depending on their boiling points and chemical properties. These results appeared as a crucial advance to progress on the understanding of silicon poisoning.

7.2.2 Introduction

Silicon species are known to be severe poisons for hydrotreatment (HDT) catalysts [2, 4, 43]. To improve the overall refining processes, the chemical structure of these molecules must be identified to understand and predict their reactivity and adverse effects. However, silicon speciation is a difficult task to perform due to the trace concentrations at which they occur in petroleum products and several pollution problems potentially taking place during the analytical procedure [14].

The presence of silicon in petroleum products is originating from the use of polydimethylsiloxanes (PDMS) which are introduced to enhance the crude oil recovery from the reservoir and as antifoaming agents to avoid emulsion phenomena in the different processes such as coking, visbreaking, steamcracking or distillation [5, 30]. The total silicon concentration determined by ICP-OES [42] or by ICP/MS [254] was ranging from several hundred $\mu g.kg^{-1}$ to some several $mg.kg^{-1}$. PDMS degrades around 300°C [10, 11, 13, 34] despite its rather good thermal stability. It will then generates many silicon compounds due to the high temperature of operation, generally around 500°C or above applied during the thermal cracking processes of hydrocarbons. As previously mentioned in the part 1 of this work, several authors have studied the thermal degradation of PDMS but mainly under inert gas [8-11]. Under these conditions, mainly cyclic siloxanes (D_n) were identified as the major degradation products of PDMS with some trace of linear siloxane (L_5) [11]. There are no reports of results under thermal cracking of hydrocarbons. Several reactions between PDMS degradation products and hydrocarbon radicals could take place under these conditions and yield a wide array of different unknown silicon species.

Chainet *et al.* have identified cyclic siloxanes (D_3-D_6) and linear siloxane (L_5) at trace levels in gasoline using GC/MS SIM (single ion monitoring) [18]. The level of total silicon content allows us to suspect that a large array of unknown silicon species could occur. However, they cannot be detected without identifying their fragment ions for structural elucidations. When using an original approach by ESI-FT-ICR/MS and Kendrick plots, more than 50 new silicon species have been characterized in the same samples by their molecular formula and double bond equivalent (DBE) [279]. However, the chemical structure of silicon species was crucial to progress on silicon speciation but cannot be determined using this technique due to the important number of possible isomers. In fact, the literature review on silicon poisoning reported that silicon species can have a very different effect on catalysts which is strongly dependent on the nature of the catalyst [32], on the experimental conditions [45] and also more specifically on the chemical nature of the silicon molecule [45]. Nuzzo *et al.* [49] have demonstrated that two silanes have different effects on Ni/Al_2O_3 catalyst for the dehydrogenation of cyclohexane. Up to now, no silicon species clearly characterized as poisons could be identified in petroleum products. Moreover, the reactivity and possible evolution of silicon species was suspected. Indeed, in some case, the silicon compounds were only analyzed after a long period of storage between the sampling site and the determination stage. This long period of storage if is not carefully controlled could modified the analytes of interest and the initial and the representative speciation could be then lost.

To characterize the PDMS degradation products under thermal cracking of hydrocarbons similarly to what happened in the refining processes, fresh and representative samples of PDMS thermally degraded with the presence of hydrocarbons were produced [20]. A pilot plant available at IFPEN was especially modified for this study and was used to produce the samples. These were directly analyzed or carefully stored in liquid nitrogen prior to the analysis to minimize the evolution of silicon species [286]. A first macroscopic analysis of the liquid fraction by µ-SEC-ICP/HRMS has demonstrated that very different silicon distribution with a wide range of molecular masses and more particularly low molecular weight compounds would occur. Some of these molecules could be then directly analyzed by GC/MS [286]. The first part of this work reported the occurrence of silicon species in the gas fraction using GC/TOFMS [309]. In the second part of the study, we will present the characterization of the liquid fraction of the samples using a multi-technical approach mainly based on gas chromatography and mass spectrometry. The aim of this study was to determine the chemical structures of silicon species known to be responsible of catalyst poisoning. The analytical strategy was described highlighting the different information provided by each technique and was then applied to the four tests operated under thermal cracking of hydrocarbons at 500°C. The occurrence of silicon compounds were presented according to the different operating conditions differing by the residence time or steam content. The silicon compounds evidenced in this paper were then discussed following their different families and the operating conditions of the degradation study. The formation and the reactivity of these species were also discussed and associated to the potential poisoning effect.

7.2.3 Materials and Methods

7.2.3.1 Silicon standards and solutions

According to previous silicon speciation studies [18, 279], a complete test mixture of 30 commercially available silicon standard molecules potentially resulting from the thermal degradation of PDMS was used in this work. Individual standards were purchased from Sigma-Aldrich (Lyon, France) and from Interchim (Montluçon, France). The raw formula, boiling points, molecular masses and the chemical structure of these silicon compounds were available in Annexe 5 and were previously reported in Chainet *et al.* [18, 279]. The storage and the complete analytical procedure to minimize silicon contamination were previously detailed in Chainet et al. [18, 279]. The test mixture was analyzed by GC/MS SIM and GC/TOFMS at a concentration of 50 mg.kg^{-1} in a mixture (50:50) of heptane (AnalaR Normapur, 99.7%) and xylene (Purex, 98.5%) respectively purchased from VWR (Fontenay sous Bois, France) and Carlo-Erba (Val De Reuil, France). This allowed obtaining the retention times and the mass spectrum (GC/TOFMS) of the commercially available silicon compounds for their future identification in the PDMS degradation samples.

7.2.3.2 Samples

To progress in silicon speciation, the production and the sampling followed by the storage of the samples were critical due to the possible evolution of silicon species. The PDMS degradation samples under thermal cracking of hydrocarbons were produced on a pilot plant [286] and then immediately stored in liquid nitrogen at -195°C to minimize the possible evolution of silicon species (Figure 7-6). All operating conditions at a temperature of 500°C were summarized in the part 1 (section 7.1) [309] and were previously described in details in

Chainet *et al.* [286]. A test was also operated at 250°C and it was demonstrated by µ-SEC-ICP/HRMS that PDMS was not degraded under these conditions [286].

7.2.3.3 Analytical strategy

The macromolecular characterization of the liquid fraction of the PDMS degradation samples was previously reported in Chainet *et al.* [286]. This fraction was also analyzed by GC-FID to follow the correct conversion of heptane and xylene, initially added to evaluate PDMS degradation under real conditions of refining and by XRF to measure the total silicon content [286].

For a complete molecular characterization of silicon species, several hyphenated techniques using GC separation coupled to various MS detectors were performed with the complementary use of FT-ICR/MS and MS^n. Figure 7-6 presents the flow chart of the multi-technical approach applied to the PDMS degradation samples and especially in this work to determine the chemical structure of silicon molecules. GC/MS in SIM (single ion monitoring) mode [18] was applied to the produced samples to characterize known silicon compounds present in the test mixture such as cyclic and linear siloxanes and also α,ω-dihydroxy polydimethylsiloxanes, well-known as thermal degradation products of PDMS [10, 13, 18]. For other silicon compounds potentially formed during PDMS degradation under thermal cracking of hydrocarbons but never characterized before, ESI-FT-ICR/MS was performed to characterize these molecules by their raw formula and double bond equivalent (DBE) [279]. However, the determination of the chemical structure of the compound was impossible because of the wide number of possible isomers. Thus, GC/TOFMS was carried out using electron ionization (EI) and chemical ionization (CI) to obtain the complete mass spectrum of these compounds and lead to their structural identification. When using the GC/TOFMS, several coelutions appeared between hydrocarbons and silicon compounds because of the complexity of the matrix. The mass spectra of these molecules were overlapped and the correct identification was not possible. To overcome these coelutions, the application of the GC-GC/TOFMS [287] with two dimensions of separation using the previous retention times obtained by GC/TOFMS allowed the characterization of these molecules by their mass spectrum. The lack of silicon compounds commercially available associated to the poor number of silicon species mass spectra in the MS library clearly showed the need to combined FT-ICR/MS with GC/TOFMS results. Using the raw formula and the double bond equivalent (DBE) determined by ESI-FT-ICR/MS and the EI and CI mass spectra provided by GC/TOFMS, the chemical structure could then be proposed and strengthen by MS^n results.

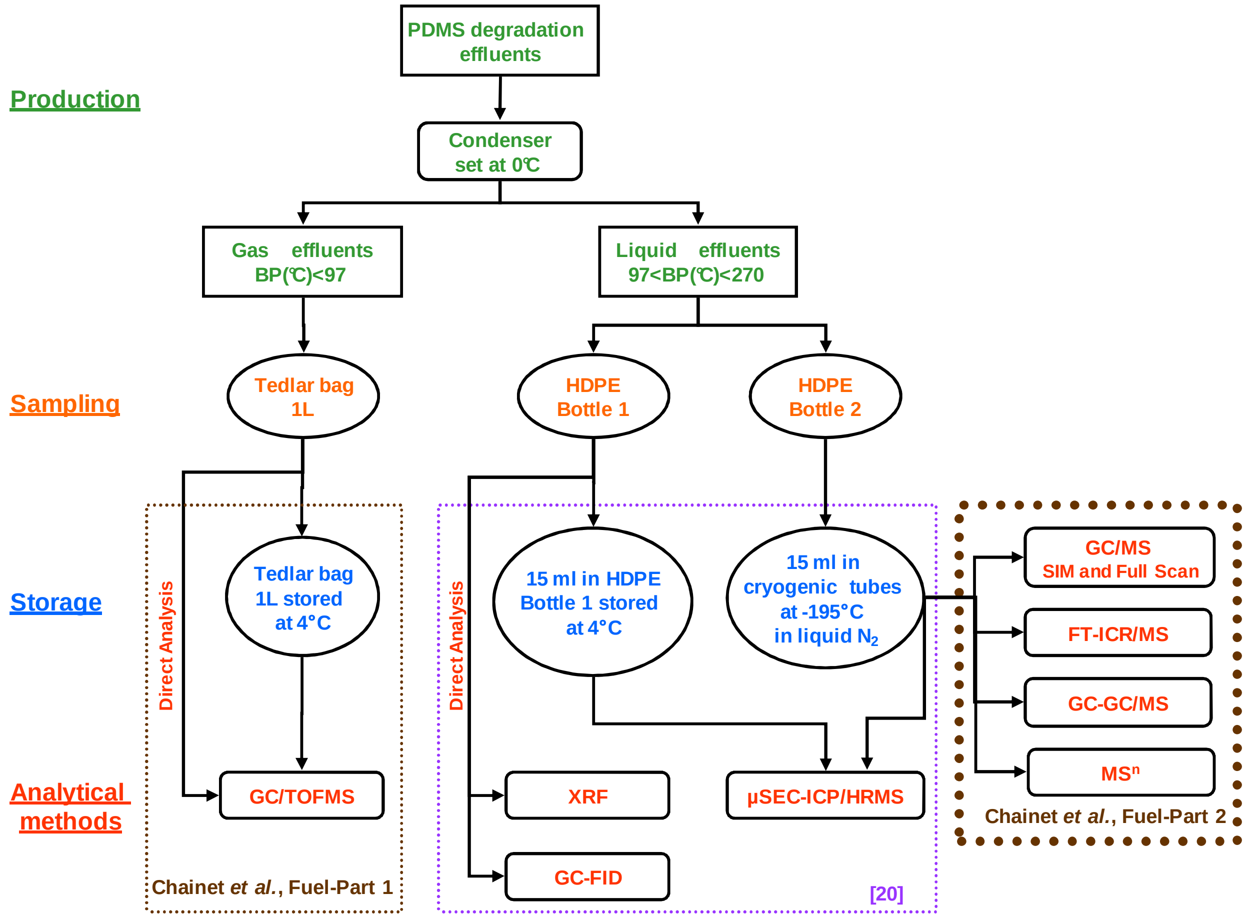

Figure 7-6. Flow chart of the analytical strategy for the effluent characterization (Adapted from [286])

7.2.3.4 Apparatus

7.2.3.4.1 GC/MS and GC-GC/TOFMS

GC/MS

Two different GC/MS analysis were performed in this study. A first approach was performed in SIM mode [18] using a gas chromatograph-mass spectrometer Thermo Scientific TRACE DSQ GC/MS (Thermo Fisher Scientific, Courtaboeuf, France). In the full scan mode, a high resolution GC/TOFMS (JEOL AccuTOF GCv, JEOL, Tokyo, Japan) was operated both in CI and EI modes. All the GC separations were achieved on a low bleed capillary column DB-5 MS UI (30mx0.25 mm i.d., 0.25 µm film thickness) from J&W Scientific (Folsom, California, United States) with the same oven temperature ramp [18, 287]. An internal standard (M_4Q) spiked at 5 mg.kg^{-1} was used to take into account the mass spectrometer variations and to achieve the relative quantification of silicon compounds. More detailed conditions about the GC/MS SIM method and the analytical precautions to minimize contaminations were previously detailed in Chainet *et al*. [18].

For the GC/TOFMS method, a volume of 0.5 µl of solution was injected through a Merlin microseal septum (Merlin Instrument Company, Half Moon Bay, CA, United States) with a 1:50 split ratio in EI and with also a splitless mode in CI [18]. The other parameters of the MS detection were similar to the one reported in the part 1 of this study (section 7.1) with only a wider scanning mass range between m/z 10 and m/z 700The GC/TOFMS using chemical ionization (CI) experiments in positive mode were carried out with CH_4 (N45-99.995%, Air liquide, France) as the reactant gas under the same chromatographic conditions to obtain the molecular mass of the molecule (MH^+). However, the observation of the protonated molecule is dependent on the efficiency of the CI and on the fragility of the silicon molecules. Several compounds could be detected through their M-15 peak, relative to a loose of CH_4 from the protonated molecule (MH^+).

GC-GC/TOFMS

The GC-GC/TOFMS experiments were carried out using an Agilent gas chromatograph 7890 (Agilent technologies, Massy, France) equipped with a Dean switch (DS) system (model G2855B, Agilent Technologies, Burwood, Australia) [295] and two flame ionization detectors (FID) coupled to a time of flight mass spectrometer (TOFMS) (AccuTOF GC, JEOL, Tokyo, Japan). The detailed operating conditions were previously reported in Chainet *et al.* [287].

7.2.3.4.2 FT-ICR/MS and MS^n

Ultra high resolution mass spectra were acquired using a LTQ-FT Ultra Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR/MS) (Thermo Fisher Scientific, Bremen, Germany) equipped with a 7 Tesla superconducting magnet and an electrospray (ESI) ion source (IonMax Thermo Fisher Scientific, Bremen, Germany). The ESI-FT-ICR/MS method with all key measurement parameters were reported in more details in Chainet *et al.* [279]. The mass ranges were successively set to m/z 50-500, m/z 100-1000 and m/z 200-2000 with 16 and 64 µscans accumulated and co-added prior to the Fourier transform to reduce electronic noise and to improve the signal to noise ratio of the resulting spectra. The FT-ICR/MS apparatus was also performed using an extended mass range up to m/z 4000 to characterize silicon compounds with a high degree of polymerization.

The MS^n experiments were performed in the same conditions as ESI-FT-ICR/MS but using the LTQ apparatus for the detection following the fragmentation. Molecules were ionized, selected with a mass tolerance of m/z 1 and fragmented using collision induced dissociation (CID) in the ion trap with a normalized collision energy ranging from 0 to 100.

7.2.4 Results and Discussion

Under thermal cracking of hydrocarbons at 500°C, various silicon compounds were produced with very different molecular masses ranging from higher residual PDMS to lower molecular silicon compounds [286]. For a molecular characterization of the liquid fraction, the multi-technical approach was applied to the four degradation tests B, C, D and E following the analytical strategy. This complete approach has allowed the determination of approximately one hundred different silicon species belonging to ten families. The test B conditions results are going to be particularly developed here since most of the silicon species highlighted in this work were characterized under these operating conditions and with the highest total silicon concentration.

7.2.4.1 PDMS degradation products already characterized

According to previous works by GC/MS in full scan mode [18], the retention times and the mass spectra of the commercially available silicon compounds and PDMS degradation products already characterized have been obtained. Based on their mass spectra, specific ions of silicon compounds already characterized were determined and allowed to analyze PDMS degradation samples using GC/MS in SIM mode. Figure 7-7 illustrates the GC/MS SIM chromatogram of the liquid fraction for the degradation test B. Cyclic siloxanes (D_3-D_{17}) were characterized as the major silicon compounds in all degradation samples representing around 95% of the total area of silicon compounds. Using the elution order based on the same repetition pattern C_2H_6OSi initially present in the PDMS, D_n compounds with a degree of polymerization above six, not commercially available, were determined. Using ESI-FT-ICR/MS, cyclic siloxanes were characterized from D_3 to D_{26} under their protonated form and using the same repetition pattern (m/z 74) (See supporting information B). Furthermore, using the extended mass range of the FT-ICR/MS, cyclic siloxanes were detected up to D_{40}. These results confirmed previous studies published in the literature which have clearly demonstrated that cyclic siloxanes (D_n) were the major silicon compounds formed during the PDMS thermal degradation under inert gas [13, 14]. Figure 7-8 displays the relative percentage in mass of D_n (D_3-D_{13}) obtained during different PDMS degradation studies [14]. The final D_n eluted molecule clearly depended on the GC oven final ramp temperature. The test E representative of PDMS degradation under coking or visbreaking processes is overlaid in red on this figure to compare our results with the literature. This mass percentage is calculated from GC/MS SIM measurements by the ratio between the area of each D_n and the sum of the D_n areas.

In all degradation studies, D_3 was the most abundant cyclic siloxane because it was the most thermodynamically stable at this temperature [301]. The relative amount of D_3 increases with the applied temperature (Figure 7-8). The relative amount of D_n decreases with the increase of the polymerization degree (n) and confirmed the previous studies reported in the literature [14]. However, this general tendency is not true for D_6 in all reports published. The formation of D_n was generated by a depolymerization mechanism with the formation of a small amount of linear siloxanes [8, 9, 11-13]. Linear siloxanes (L_2-L_5) were also characterized in our work and were further discussed in the next section. In our study, the relative amount of D_n when n is above 6, is less intense than in the other works. This result could be explained by two reasons. First, the applied temperature was the most important parameter and clearly influenced the relative amount of cyclic siloxanes. In fact, the cyclization of the D_n is less favoured for high degree of polymerization. Secondly, the presence of hydrocarbons, never tested during PDMS thermal degradation, could influence the reactivity of PDMS degradation products to form other silicon molecules never characterized before.

Under thermal cracking conditions of hydrocarbons, the different conditions of the process did not seem to influence the relative abundance of D_n. Figure 7-9 displays the relative percentage of the different D_n for the tests operated at 500°C in the presence of hydrocarbons. No significant differences on the relative abundance of D_n were observed for the different PDMS degradation tests up to D_9. For tests B and C conditions, operated with short residence times, the relative area of D_n (for $n>9$) is more important than for the tests D and E when operating with long residence times. This result demonstrated that the PDMS is less degraded under short residence times and confirmed the previous trend observed using µ-SEC-ICP/HRMS [286].

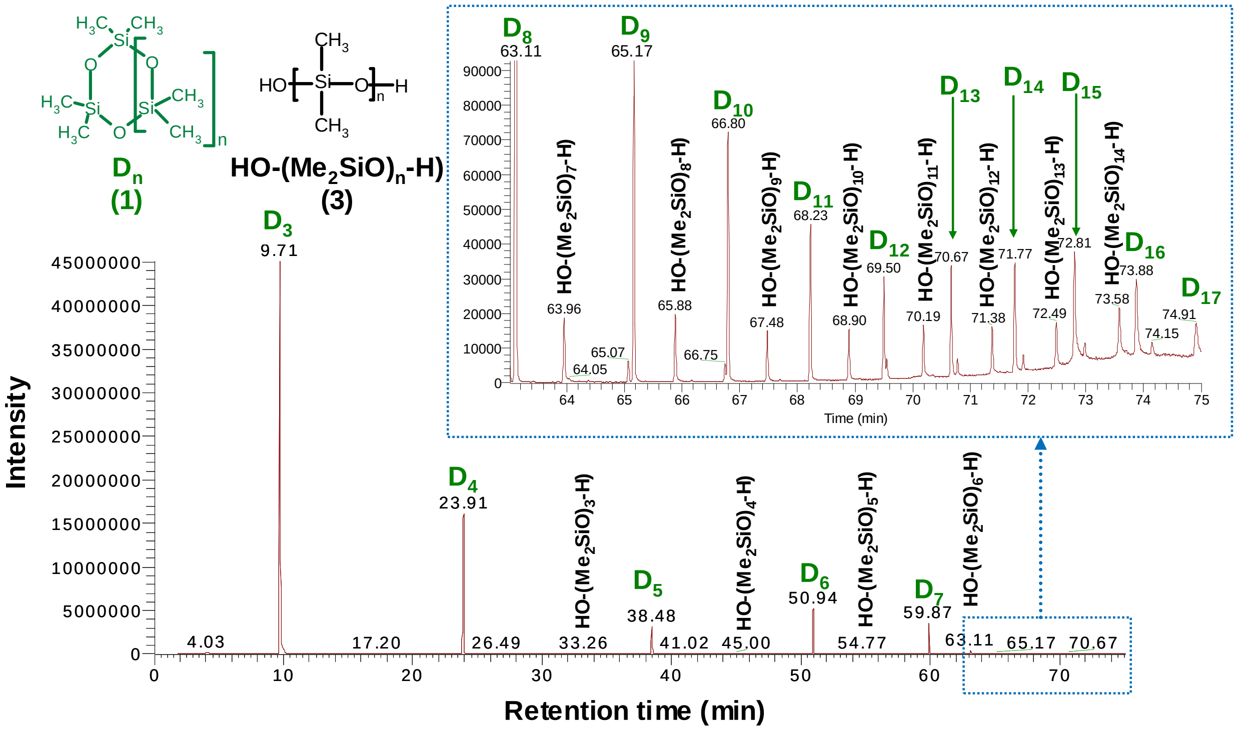

Figure 7-7. GC/MS SIM chromatogram obtained during the analysis of the liquid fraction of the degradation test B (500°C, short residence time and 50% in mass of steam) with a zoom inset between 63 and 75 minutes showing the characterization of α,ω-dihydroxy polydimethylsiloxanes (Si_n) eluted after each (D_{n+1}) cyclic siloxane (D_n)

Thanks to their mass spectra previously obtained by Varaprath *et al.* [90] and the repetition pattern (C_2H_6OSi), α,ω-dihydroxy polydimethylsiloxanes were also characterized. A α,ω-dihydroxy polydimethylsiloxane with n Si atoms is eluted between the (n+1) cyclic siloxane and the (n+2) cyclic siloxane (Figure 7-7) [90]. A zoom inset between 63 and 75 minutes of the GC/MS SIM chromatogram clearly illustrates the characterization of these species (Figure 7-7).

α,ω-dihydroxy polydimethylsiloxanes (monomer to trimer) were already characterized during PDMS degradation under environmental conditions with very long residence time around several months [110]. In our degradation tests, α,ω-dihydroxy polydimethylsiloxanes with a degree of polymerization up to 14 were highlighted by GC/TOFMS. These molecules were preferentially formed in the presence of steam following the hydrolysis of the initial PDMS (Figure 7-13) [306]. They were also detected in test E (absence of steam) at trace levels when using FT-ICR/MS detection capacities due to the high sensitivity of the technique. Their presence in the tests in the absence of steam can be explained by the initial presence of water (initial concentration <150 ppm) in the mixture of heptane and xylene. α,ω-dihydroxy polydimethylsiloxanes are known to be very reactive due to the presence of the hydroxy groups at the end of the chain which can induce the formation of linear siloxanes (L_n) by condensation [302, 309]. The condensation can be also observed at the surface of the Al_2O_3 catalytic support as previously proposed in the part 1 for the trimethylsilanol (TMSOH) formation [309]. This reaction can form modified silica structure at the surface of the catalysts and involves their deactivation [50].

As previously mentioned, linear siloxanes (L_2-L_5) were detected at trace levels using GC/MS SIM and only during PDMS degradation tests during the long residence time conditions (tests D and E) (Figure 7-13). These silicon compounds were formed under the coking or visbreaking conditions and preferentially in the absence of steam. The linear siloxane hexamethyldisiloxane (L_2) was recognized to be a severe poison for Pt and Pd catalysts [64-67] but was characterized for the first time in petroleum products.

Using results from GC/MS SIM, other unknown silicon compounds (never characterized before) appeared to be present in the samples due to the detection of specific ions but their chemical structure could not be determined. Only silicon compounds previously known by their mass spectrum can be detected using this method. The use of FT-ICR/MS will provide the characterization by their raw formula of these unknown compounds never characterized before during PDMS degradation.

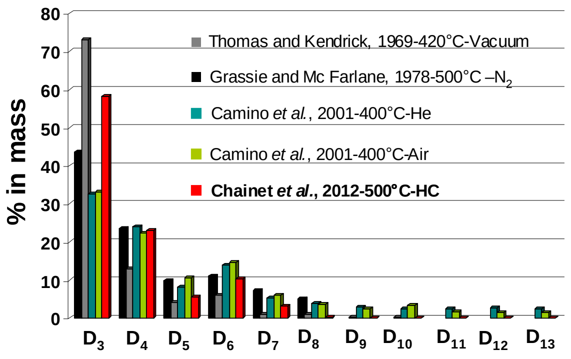

Figure 7-8. Cyclic siloxanes (D_n) distribution observed during PDMS thermal degradation at different temperature (in mass percentage)

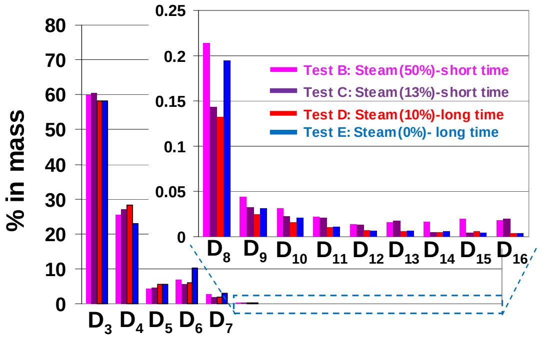

Figure 7-9. Cyclic siloxanes (D_n) distribution observed during the four PDMS thermal degradation studies (Tests B, C, D and E) under thermal cracking of hydrocarbons at 500°C (in mass percentage)

7.2.4.2 Characterization of silicon species never reported during PDMS degradation

7.2.4.2.1 Characterization by FT-ICR/MS

Compounds with four atoms of silicon were chosen to be illustrated because all ten molecule families were detected in these samples. Masses (measured and theoretical), mass error, relative intensity, formula $[M+H]^+$ and double bond equivalent (DBE) for Si_4 compounds characterized in these PDMS degradation tests are detailed in Table 7-6. Similarly to GC/MS, the same repetition pattern C_2H_6OSi (m/z 74.01824) was highlighted using ESI-FT-ICR/MS and allowed to easily assign the other compounds of the family. All other silicon compounds characterized with a different degree of polymerization were available in the supporting information B (Annexe 6-Table A2).

The relative intensity of Si_4 compounds was calculated using the silicon compound D_4 at m/z 297.08243 because it was the compound with the most abundant intensity. However, ESI-FT-ICR/MS did not allow to give information about the relative quantity of silicon compounds [279]. The relative quantification of these molecules will be established using GC/TOFMS in the next section. All Si_4 compound masses were measured with a mass accuracy below 0.17 ppm and allowed an assignment of the raw formula with the number of unsaturations (DBE). The number of unsaturations is ranged from 0 to 2 and confirmed the previous results using ESI-FT-ICR/MS that have demonstrated the occurrence of silicon compounds with several unsaturations in naphtha and gasolines originating from steam cracking process [279]. However, the determination of the chemical structure was very difficult to achieve since several isomers could be possible. Thanks to their raw formula, they were searched for using GC/TOFMS. Combining the molecular masses obtained by ESI-FT-ICR/MS and the fragmentation pattern provided by the EI mass spectrum, the chemical structure may be proposed.

Table 7-6. List of Si_4 silicon ions with their masses (measured and theoretical), mass error, relative intensity, formula $[M+H]^+$ and double bond equivalent of the molecule (DBE) for the test B (500°C, short residence time and 50% in mass of steam) obtained with an ESI-FT-ICR/MS acquisition (64 µscans and resolution of 200,000 at m/z 400). The molecules are ranged by decreasing the relative intensity

Measured Mass	Theo. Mass	Mass error (ppm)	Relative Intensity	Formula $[MH]^+$	DBE
297.08243	297.08244	-0.01	1.000	$C_8 H_{25} O_4 Si_4$	1
299.06169	299.06170	-0.01	0.413	$C_7 H_{23} O_5 Si_4$	1
327.09299	327.09300	-0.01	0.297	$C_9 H_{27} O_5 Si_4$	1
315.09306	315.09301	0.17	0.251	$C_8 H_{27} O_5 Si_4$	0
313.11378	313.11374	0.04	0.058	$C_9 H_{29} O_4 Si_4$	1
281.05116	281.05114	0.02	0.042	$C_7 H_{21} O_4 Si_4$	2
329.07234	329.07227	0.06	0.026	$C_8 H_{25} O_6 Si_4$	1
325.11372	325.11374	-0.02	0.016	$C_{10} H_{29} O_4 Si_4$	1
343.12434	343.12431	0.04	0.012	$C_{10} H_{31} O_5 Si_4$	0
357.10351	357.10357	0.17	0.007	$C_{10} H_{29} O_6 Si_4$	1
283.03053	283.03041	0.12	0.005	$C_6 H_{19} O_5 Si_4$	2

7.2.4.2.2 Characterization by GC/TOFMS and GC-GC/TOFMS

The liquid fraction of PDMS degradation samples was analyzed by GC/TOFMS in order to obtain their complete mass spectrum and give structural information. Heptane and the three isomers of xylene, initially present as source of hydrocarbons, were converted in various hydrocarbons, ranging from C_1 to C_{15} which can coelute with silicon compounds [286]. With the presence of highly concentrated cyclic siloxanes (D_n), many other silicon compounds at low concentrations were characterized by their mass spectra. Figure 7-10-a illustrates a zoom of the GC/TOFMS chromatogram between 36 and 40 minutes to demonstrate the coelution between a silicon and an oxygenated compounds at 37.12 minutes. The resulting mass spectrum is presented in the Figure 7-10-b. The mass spectrum of the silicon compound is composed of major ions at m/z 163, 325 and 341 whereas the oxygenated compound has major ions at m/z 91, 107 and 122. These molecules cannot be identified and their relative quantification is therefore biased. To resolve these coelutions and allow the characterization of silicon compounds, GC-GC/TOFMS has been investigated.

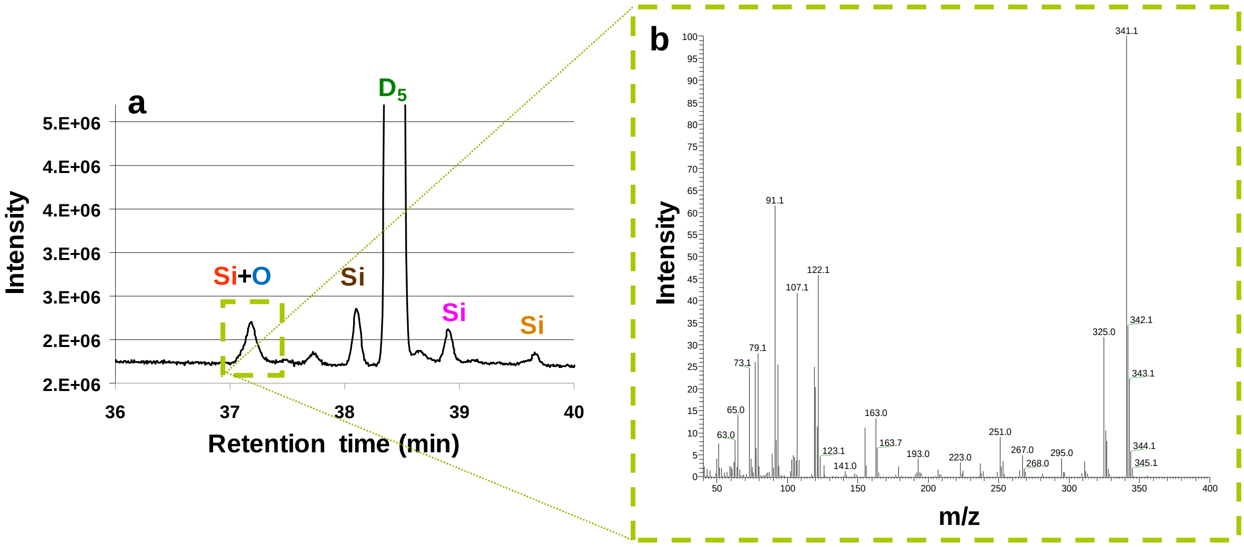

Figure 7-10. (a) Zoom of the GC/TOFMS chromatogram between 36 and 40 minutes illustrating the coelution between a silicon compound and an oxygenated compound at 37.12 minutes (I=4.91) and (b) its mass spectrum obtained by GC/TOFMS obtained for the PDMS degradation test B (500°C, short residence time and 50% in mass of steam)

To facilitate the determination of the time of cuts to transfer of the coeluted molecules on the second dimension coupled to the TOFMS, retention indices (I) were calculated based on the cyclic siloxanes (D_n) as reference molecules in order to have a unique value of retention using GC for each silicon compound. This calculation was detailed in the supporting information B for further details [287]. Table 7-7 presents the seven silicon compounds coeluted with hydrocarbon, oxygenated, or also other silicon compounds. Seven cuts were carried out and were successfully resolved. However, the cut with the two silicon compounds at 35.61 min displays an improvement in terms of resolution but gave access to two similar mass spectra, preventing identification. For all the others, the target silicon compounds were clearly separated from the other molecule due to the different selectivity of the second dimension of separation. The mass spectrum of each silicon compound is then clearly obtained. However, the molecular identification is hard to achieve with the EI mass spectrum exclusively and a combination of the ESI-FT-ICR/MS information (raw formula and DBE), GC/TOFMS results in CI and MS^n must be applied.

Table 7-7. GC/TOFMS retention times and cuts defined by GC-GC/TOFMS for the 7 target silicon compounds coeluted using GC/TOFMS experiments and for reference molecules obtained for the PDMS degradation test B (500°C, short residence time and 50% in mass of steam)

GC/MS t_R (min)	Molecules	Theoretical t_R (min) in GC-GC/TOFMS	Cuts used in GC-GC/TOFMS
1.97	TMSOH	3.90*	3.81-4.00
3.38	L_2	6.43*	6.35-3.51
9.71	D_3	15.23*	15.00-15.38
15.95	$Si+C_9$	22.82	22.50-23.00
16.51	$Si+C_{10}$	23.48	23.20-23.80
17.40	$Si+C_{10}$	24.31	24.0-24.60
22.72	$Si+Ar(C_9)$	27.92	27.60-28.60
23.91	D_4	31.78*	31.40-32.00
24.99	$Si+Ar(C_{10})$	33.01	32.80-33.50
35.61	Si+Si	42.99	42.20-43.20
37.12	Si+O	44.26	43.90-45.80
38.48	D_5	45.50*	
43.09	M_4Q	47.98	47.40-49.20
50.92	D_6	57.82*	57.40-58.10

Ar: aromatic;* TMSOH, L_2 and D_n are the reference molecules for the calculation of retention indices

7.2.4.2.3 Combination of the results obtained by ESI-FT-ICR/MS and GC/TOFMS

By combining the molecular mass provided by the exact mass measurement using ESI-FT-ICR/MS and hypothesis on the molecule fragmentation under EI based on model silicon compounds, silicon species were searched for in the GC/TOFMS chromatograms. Figure 7-11 presents four mass chromatograms (a-m/z 267, b-m/z 281, c-m/z 327 and d-m/z 295) which illustrate the detection of the Si_4 molecules previously characterized using ESI-FT-ICR/MS. Their molecular formula obtained by ESI-FT-ICR/MS was confirmed by GC/TOFMS under its M-15 peak. Adding the EI mass spectrum information concerning the fragmentation of the molecule, the raw formula was assigned to each silicon compound using the same colour and number as in the rest of the paper (Figure 7-13).

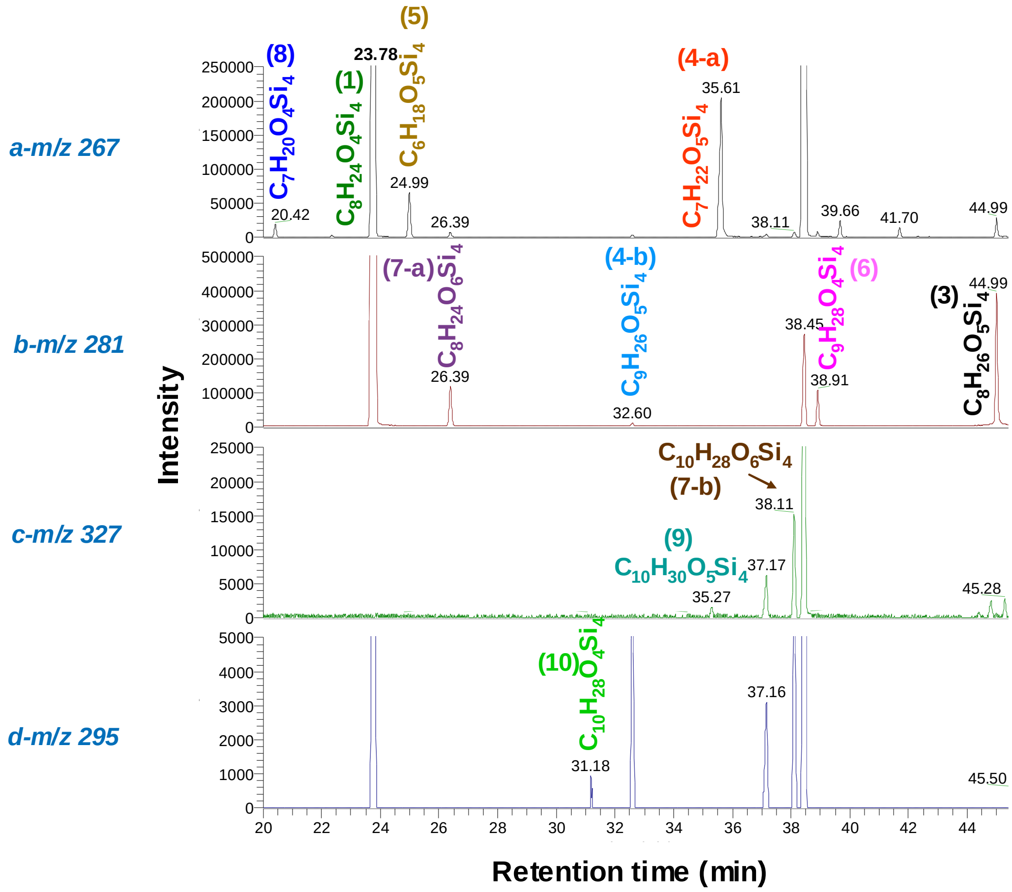

Figure 7-11. GC/TOFMS extracted ion chromatogram (EIC) m/z 267 (a), m/z 281 (b), m/z 327 (c) and m/z 295 (d) obtained for the TIC chromatogram of the test B (500°C, short residence time and 50% in mass of steam). The numbers and colors of the different families are indicated as the same as in Figure 7-13. Linear siloxanes (2) were not detected in the test B

An example was presented for the structural identification of $C_7H_{22}O_5Si_4$ detected at m/z 299.06169 under its protonated form using ESI-FT-ICR/MS with a mass accuracy of 0.01 ppm and with one unsaturation (Table 7-6). Figure 7-11 illustrates the CI mass spectrum obtained for the Si_4 molecule at 35.61 min using GC/TOFMS. The (M-15) peak at m/z 283.0311 was originated from the first elimination of CH_4 from the protonated molecule (MH^+) (similarly to the fragmentation of D_4, see supporting information D-Annexe 6-Table A4). The peak m/z 266.997 (M-31) fit to the second elimination of CH_4, which is already demonstrated in the literature for the fragmentation of cyclic siloxanes (D_n) [107, 243]. The peak observed in CI mass spectrum (Figure 7-11) at m/z 281.0511 (M-17) match to the loss of 18 from the MH^+ peak which is probably relative to the elimination of water. Therefore, the cyclic siloxane has methyl groups linked to silicon but also one hydroxy group following the determined molecular mass. The chemical structure of this compound was strengthened as heptamethylhydroxyl cyclotetrasiloxane using MS^2 experiments (see supporting information

C-Annexe 6). The other members of the family can be easily assigned thanks to the repetition pattern C_2H_6OSi using the exact mass by FT-ICR/MS (m/z 74) and the retention time by GC/TOFMS as already processed in [279] and in [18].

The described procedure for the identification of the compounds by their chemical structure was detailed for heptamethylhydroxyl cyclotetrasiloxane (4-a) (See supporting information C-Annexe 6). This complete approach was applied to all Si_4 compounds in order to confirm the proposed chemical structure according to their molecular mass, DBE and EI and CI mass spectra. Their mass spectra were available in Annexe 7. Then, the other compounds of a family were characterized using the repetition pattern C_2H_6OSi. Among the ten families of silicon compounds characterized (included linear siloxanes) in PDMS degradation samples, seven families were clearly characterized by their chemical structure and strengthened by MS^n. The details of CI and EI fragment ions and MS^n fragments for all silicon molecules were available in the supporting information D (Annexe 6-Table A4).

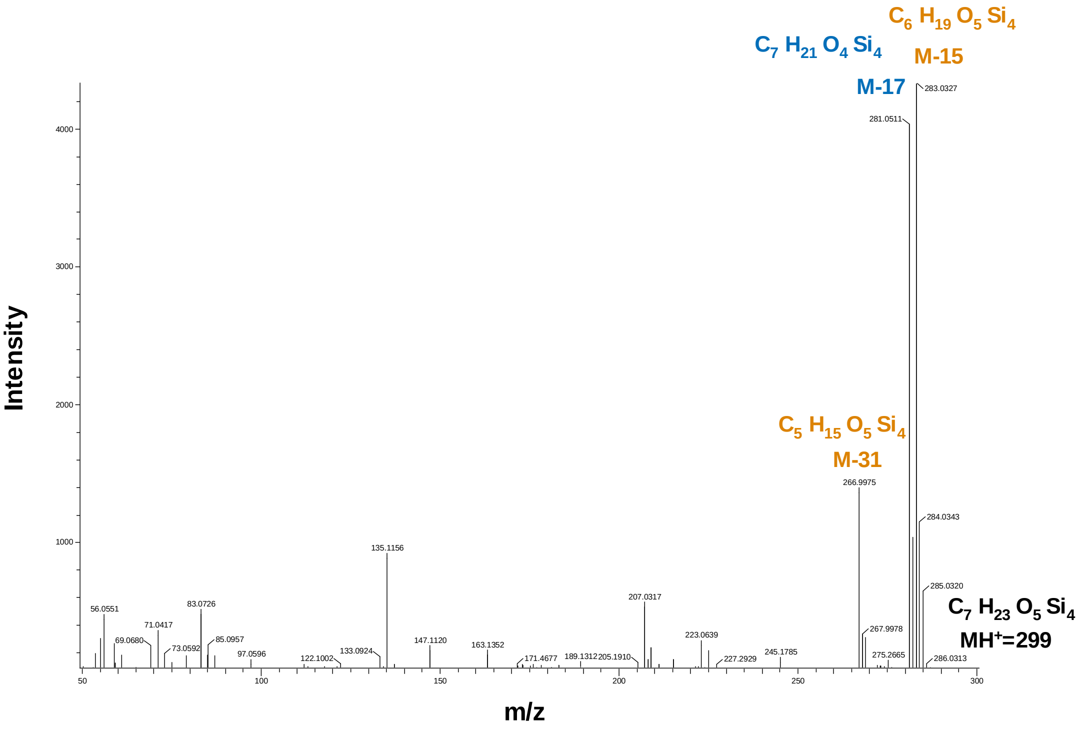

Figure 7-12. CI mass spectrum of the Si_4 compound eluted at 35.61 minutes on the GC/TOFMS chromatogram obtained for the degradation test B (500°C, short residence time and 50% in mass of steam). The EI mass spectrum is available on the supporting information (Annexe 6-Section C-Figure A 4)

7.2.4.3 Formation of silicon species never characterized during PDMS degradation

As previously mentioned, cyclic siloxanes were the major silicon compounds originating from PDMS thermal degradation with a relative area of around 95% of the total area of silicon species. This part is focused on the new silicon species never characterized during PDMS degradation samples and especially in the presence of hydrocarbons. In fact, the total relative area of these molecules are ranging from 0.5 to 4.5 % of the sum of all silicon species areas depending on the operating conditions and clearly appeared at trace levels. Figure 7-13 displays the relative area of silicon species following the tests B, C, D and E. For each test, the relative area of each compound is normalized to the sum of the relative areas (except D_n for a better visualization of the results) and plotted on the graph. To understand the influence of the operating conditions, the formation of these silicon molecules was discussed following the residence time (short and long) and the steam content. As most of these new silicon species were totally unknown before this work, no information about their influence on catalytic activity was available.

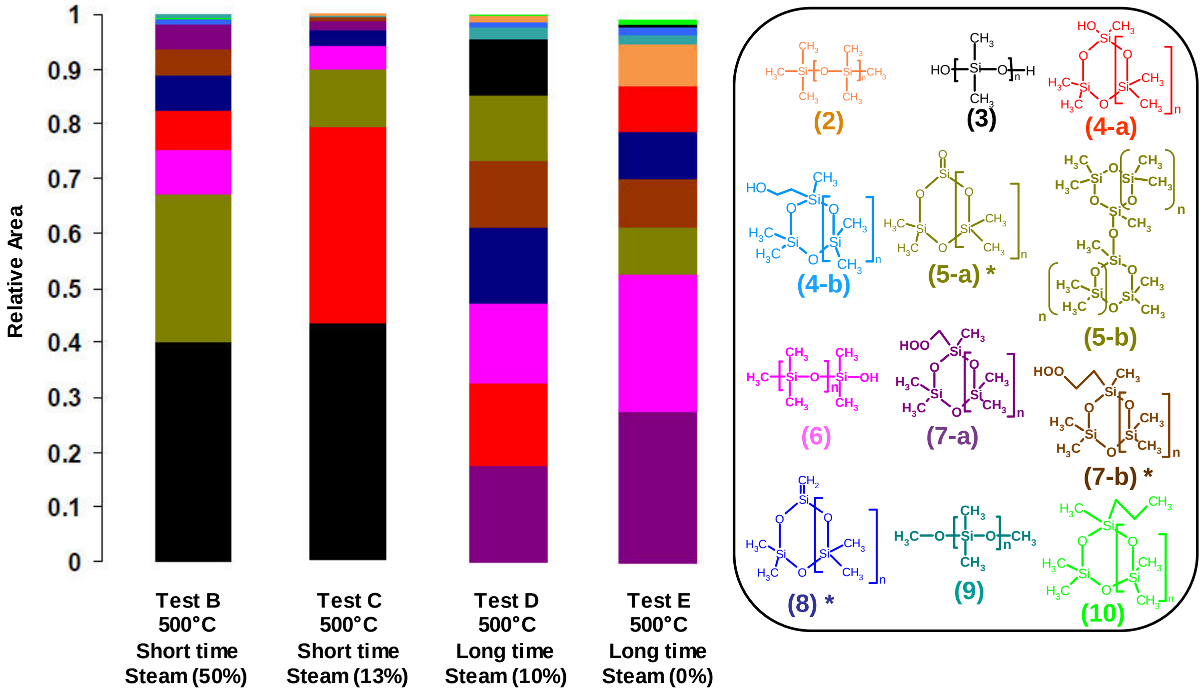

Figure 7-13. Relative distribution of silicon compounds family (except D_n) observed during the four PDMS thermal degradation tests (B, C, D and E) at 500°C. Silicon species are illustrated by their chemical structure previously determined using colours. For this molecule (*), the structure is proposed based on the raw formula, DBE, EI mass spectrum (fragmentation) but MSn experiments are not sufficient to strengthen the structure. The histograms are displayed by increasing the relative areas in each degradation test.

Hydroxymethyl cyclic siloxanes (4-a: Si_3-Si_9) were characterized in all degradation tests with a higher relative concentration under short residence time and with 13% of steam (Test C). The Si_4 molecule was previously evidenced by Sommerlade *et al.* [107] during the reaction between D_4 and OH radicals. The adsorption of the OH groups at the surface of the alumina support could be similar than α-hydroxy,ω-methyl polysiloxanes and formed silica structure which induced a catalytic deactivation [309]. The family methyl(hydroxyethyl) cyclic siloxanes (4-b: Si_3-Si_9) was formed under coking or visbreaking conditions and preferentially in the absence of steam (test E) but with a lower relative area than the family 4-a. Sommerlade *et al.* [107] have already identified heptamethyl(hydroxymethyl) cyclotetrasiloxane during the reaction between D_4 and radicals OH but with one lower CH_2 alkylation. This result may suppose a reactivity of PDMS degradation products with carbon radicals coming from the hydrocarbon matrix. This molecule was constituted of ramifications different than methyl groups on silicon atoms. This issue was also observed for two other silicon compounds (7-b and 10 families).

Cyclic silanone (5-a: Si_3-Si_{10}) or bis(cyclosiloxanyl)siloxane (5-b: Si_6-Si_{10}) were detected with a high abundance in the test B under short residence time and 50% of steam (Figure 7-13). Similarly to α,ω-dihydroxy polydimethylsiloxanes and methylhydroxyl cyclic siloxanes, the presence of steam seems to promote their formation. For a number of 6 Si atoms or above, a bis(cyclosiloxanyl)siloxane could be formed by the condensation of two hydroxylmethyl cyclic siloxane (4-a) previously highlighted in our degradation tests (Figure 7-13). In fact, the stability of the cycle is raised for three silicon atoms and allowed the formation of the two cyclic siloxanes linked by an oxygen atom [310]. The bis(heptamethylcyclotetrasiloxanyl)siloxane ($C_{14}H_{42}O_9Si_8$) was confirmed by MS^2. Moreover, the mass spectrum obtained using GC/TOFMS in EI perfectly fitted with the previous one obtained by Sommerlade *et al.* [107]. For this family, another chemical structure with a DBE of 2 (5-a) can be proposed for a number of silicon atoms under six because the previous structure cannot be formed (Figure 7-13). According to raw formula, DBE, EI mass spectrum, the hexamethyl cyclic silanone was proposed but this structure wasn't strengthened by MS^2 and was known to be very unstable due to the silanone group [311] (Figure 7-13). This molecule could be formed by the condensation of dihydroxy cyclic siloxane detected at a very low intensity using ESI-FT-ICR/MS.

α-Hydroxy,ω-methyl polysiloxanes (6: Si_1-Si_8), including the trimethylsilanol (TMSOH), were also highlighted in all PDMS degradation samples. These molecules were preferentially produced under long residence times (tests D and E) (Figure 7-13) and were previously characterized by Stewart *et al.* [312] during the reaction of linear siloxanes (L_n) with OH radicals in atmospheric studies. This reaction can explain the presence of this type of molecule during PDMS thermal degradation. The amount of L_n is more important during PDMS degradation tests under long residence time. This trend was similar for α-hydroxy,ω-methyl polysiloxanes and could potentially confirm their formation (Figure 7-13). α-hydroxy,ω-methyl polysiloxanes were never tested during catalyst poisoning but similar condensation as α,ω-dihydroxy polydimethylsiloxanes or hydroxymethyl cyclic siloxane on the catalytic support could occur [309].

The family indicated as number 7 (Si_3-Si_6) was composed of two different silicon compounds (7-a and 7-b) and were formed in all degradation tests. The first hydroperoxy cyclic siloxane (7-a) was characterized using GC/TOFMS in EI mode by the peak M-47. This peak was probably relative to the elimination of the methylhydroperoxy group (see supporting information D, Annexe 6-Table A4) and was also strengthen by MS^2. Considering the silicon chemistry, this chemical structure was the most possible. According to the same hypothesis, the family 7-b is probably also hydroperoxycyclic siloxane with a different number of CH_2 alkylation than the family 7-a but the chemical structure cannot be analyzed by MS^2 measurement due to sensitivity issues. Under evaluated visbreaking or coking conditions (long residence time), hydroperoxy cyclic siloxane were preferentially produced. The Si_4 species was already highlighted by Sommerlade *et al.* [107] during D_4 and OH radicals reactions. Moreover, Camino *et al.* [10] and Dvornic [301] have already proposed a mechanism for the formation of these molecules during PDMS thermal degradation through the occurrence of side-chain peroxides. This molecule appears as very reactive due to the presence of the hydroperoxy function and strongly affects the performance of HDT catalysts.

The family number 8 (Si_3-Si_{10}) was mainly characterized in degradation tests B and D. The presence of steam seems to increase the quantity of these compounds. The compounds of this family was characterized as cyclic siloxane with a DBE of 2 but the MS^4 experiments performed on the Si_4 molecule do not allow to distinguish their chemical structure from one of the D_4. However, the MS^4 experiments allowed to eliminate various structures initially proposed and that were matching with the raw formula. Due to the presence of three silicon atoms, the repetition pattern C_2H_6OSi, the DBE of 2 and the raw formula combined to the detection of the ion at m/z 267 (fitted to M-13 peak) in the GC/TOFMS using EI and CI, the proposed structure could contain a sylene function ($Si{=}CH_2$) (Figure 7-13). Even if this function is known to be very unstable [311], the proposed chemical structure was likely to occur.

Dimethoxy polysiloxanes (9: Si_2-Si_8) and (methylpropyl) cyclic siloxanes (10: Si_3-Si_5) were formed under coking or visbreaking conditions and preferentially in the absence of steam (test E) (Figure 7-13). The chemical structures of these two families were strengthened by MS^2 experiments. Similarly to the methyl(hydroxyethyl) cyclic siloxanes (4-b) and (hydroperoxypropyl) cyclic siloxane (7-b), the chemical structure of the silicon species family 10 could be potentially explained by the reactivity of carbon radicals with PDMS degradation reaction products.

A very large array of silicon species never reported before were characterized during PDMS degradation under thermal cracking of hydrocarbons at 500°C. The presence of steam increases the relative amount of α,ω-dihydroxy polydimethylsiloxanes, methylhydroxy cyclic siloxanes, α -hydroxy,ω-methyl polysiloxanes and bis(cyclosiloxanyl)siloxane. However, cyclic silanones and sylene cyclic siloxanes were known to be very unstable but these chemical structures were the most plausible. The residence time has also a great influence because dimethoxy polysiloxanes, (hydroperoxy) cyclic siloxanes, methyl(hydroxyethyl) cyclic siloxanes, linear polysiloxanes and (methylpropyl) cyclic siloxanes were only formed under the evaluated coking or visbreaking conditions (long residence time).

7.2.5 Conclusions

To progress on the understanding of silicon poisoning, the structural characterization of silicon species originating from the thermal degradation of PDMS used as an antifoaming agent is essential. PDMS degradation samples were produced under thermal cracking of hydrocarbons at 500°C using a pilot plant. A direct analysis and a careful storage of the samples in liquid nitrogen allowed the application of powerful analytical methods mainly based on GC and MS to characterize silicon species.

For commercially available silicon compounds and PDMS degradation products already known, GC/MS SIM was applied to the sample but unknown species cannot be determined without information about their fragment ions. For silicon compounds never characterized before, the use of FT-ICR/MS gave access to the raw formula and to the DBE of each silicon compounds. To obtain the structural identification, GC/TOFMS was carried out to give access to the mass spectrum in EI and CI but several coelutions were observed. These coelutions were successfully resolved using GC-GC/TOFMS. However, due to the lack of commercially available silicon species and the poor number of silicon species mass spectra in the MS library, the characterization of these compounds was not sufficient. Thus, combining the mass spectrum in EI and CI with the FT-ICR/MS data, the chemical structure can be proposed. Most of them were clearly strengthened by MS^n.

This study confirmed that cyclic siloxanes (D_n) were the major PDMS degradation compounds (around 95%) even in the presence of hydrocarbons in all degradation studies. The rest of the silicon compounds (<5%) showed a wide array of silicon species never characterized before during PDMS degradation: α,ω-dihydroxy polydimethylsiloxanes, (methylhydroxy) cyclic siloxanes, bis(cyclosiloxanyl)siloxane, α-hydroxy,ω-methyl polysiloxanes, dimethoxy polysiloxanes, (hydroperoxy) cyclic siloxane, methyl (hydroxyethyl) cyclic siloxanes, linear siloxanes and (methylpropyl) cyclic siloxanes. In the presence of steam, ω-dihydroxy polydimethylsiloxanes, (methylhydroxy) cyclic siloxanes, bis(cyclosiloxanyl)siloxane, α-hydroxy,ω-methyl polysiloxanes were preferentially formed. Under evaluated coking or visbreaking conditions (long residence time in the absence of steam), dimethoxy polysiloxanes, (hydroperoxy) cyclic siloxane, methyl (hydroxyethyl) cyclic siloxanes, linear siloxanes and (methylpropyl) cyclic siloxanes were mainly characterized. Cyclic silanone and sylene cyclic siloxanes were known to be unstable but the proposed chemical structure appeared to be likely to occur. These species demonstrated structure including potential reactive groups (hydroxy, peroxy, methoxy) able to react with HDT catalysts and cause a deactivation.

The relative abundance of these new silicon species demonstrated that operating conditions have a great influence on the PDMS degradation compounds and especially under thermal cracking of hydrocarbons. Therefore, silicon species characterized in petroleum products will be different and will depend on the operating processes. The occurrence of the repetition pattern C_2H_6OSi initially present in the PDMS structure was also recovered for all silicon families. Silicon compounds have a number of silicon atoms ranging from one to forty and clearly demonstrated that silicon will distillate in all petroleum cuts from light gas petroleum cuts to heavy cuts through the different chemical structures characterized in this work. The discovery of these silicon compounds never reported before during PDMS thermal degradation considerably improves the knowledge of silicon speciation in petroleum products. This major advance for the oil and gas industry is essential to progress on the understanding of HDT catalyst poisoning by silicon.

Conclusion générale de la partie C

La troisième partie avait pour but de réaliser une spéciation du silicium dans des échantillons produits dans des conditions de dégradation du PDMS représentatives de celles appliquées dans les différents procédés de raffinage. La modification d’une unité pilote disponible au sein d’IFPEN a permis la production d’échantillons « frais » qui ont pu être analysés par une stratégie analytique multi-technique soit directement après leur production soit après un stockage adapté pour minimiser l’évolution possible des espèces silicées. Cette approche inédite associant une expérimentation pilote et une stratégie analytique multi-technique a démontré tout son potentiel pour parvenir à établir la caractérisation de plus d’une centaine de composés silicés issue de la dégradation du PDMS.

Dans un premier temps, nous avons confirmé la stabilité thermique du PDMS même en présence d’hydrocarbures. A 250°C, les résultats ont démontré que l’agent antimousse ne se dégradait pas. Néanmoins, il est important de souligner que l’ajout de vapeur d’eau dans ces conditions pourrait probablement conduire à la dégradation du PDMS mais avec des temps de séjour beaucoup plus longs, similairement aux études effectuées dans l’environnement.

Dans un second temps, les résultats ont montré que la dégradation du PDMS dans des conditions de craquage thermique généralement effectué à 500°C était dépendante des conditions appliquées. La caractérisation macroscopique des effluents a montré la présence de PDMS non dégradé, de polymères silicés intermédiaires et de composés silicés de bas poids moléculaire à différentes teneurs en fonction des conditions appliquées. La présence du silicium va donc être effective dans toutes les coupes pétrolières, des fractions gaz aux coupes les plus lourdes. Les formes chimiques retrouvées sont différentes selon les procédés de raffinage mis en œuvre. Les siloxanes cycliques (D_n) ont été confirmés comme composés majoritairement formés (environ 95% des produits formés) et cela quelques soient les conditions de dégradation.

Pour la première fois, une multitude de composés silicés, pour la plupart jamais caractérisée, a été mise en évidence en très faible quantité par rapport aux D_n (environ 5% des produits formés selon les conditions). Cependant, la présence de groupes réactifs (hydroxy, méthoxy, hydropéroxy...) au sein des molécules mises en évidence donne une importance accrue à ces molécules pour les questions d'empoisonnements des catalyseurs de l'industire pétrolière. Ces molécules vont donc être susceptibles d'interagir avec les catalyseurs, *via* une réaction possible entre les groupements réactifs et le support catalytique (Al_2O_3) et donc entraîner un empoisonnement. Mon travail de thèse a en outre permis de montrer que la formation de ces composés va dépendre de la teneur en vapeur d'eau et du temps de séjour. En présence de vapeur d'eau, les composés de type α,ω-dihydroxy polydiméthylsiloxanes, méthylhydroxy siloxanes cycliques, bis(cyclosiloxanyl) siloxane and α-hydroxy,ω-méthyl polysiloxanes ont été majoritairement observés. Au contraire dans des conditions proches de celles de la cokéfaction ou de la viscoréduction, des silanes, des diméthoxy polysiloxanes, des hydropéroxy siloxanes cycliques, des méthyl(hydroxyéthyl) siloxanes cycliques, des siloxanes linéaires et des méthylpropyl siloxanes cycliques ont été principalement caractérisés.

Concernant les hypothèses émises sur la possible évolution des espèces silicées, l'observation de la condensation du triméthylsilanol (TMSOH) pour former de l'hexamethyldisiloxane (L_2) a été mise en évidence lors de l'analyse de la fraction gazeuse des effluents. Ce résultat montre donc la nécessité d'un stockage adapté et d'une analyse rapide pour la spéciation du silicium dans le but de minimiser l'évolution des espèces silicées. Cette évolution doit être également étudiée dans la fraction liquide des échantillons produits afin de proposer des solutions adaptées pour être sûr d'identifier les molécules silicées réellement présentes au moment de l'empoisonnement.

La spéciation du silicium a donc été établie au cours de ma thèse et apporte des réponses cruciales pour l'industrie pétrolière. La diversité des composés retrouvés par leur degré de polymérisation (C_2H_6OSi) et par leur différente forme chimique, constitue la base des futurs travaux à entreprendre afin de tenter de limiter l'empoisonnement des catalyseurs utilisés dans les différentes coupes pétrolières, des phases gaz (C_1-C_4), naphta et essences (C_5-C_{10}) aux coupes les plus lourdes (gazole, huiles lourdes). Dans ce chapitre, nous avons commencé à mettre en évidence les composés silicés connus pour être des poisons des catalyseurs. Néanmoins, peu de tests d'empoisonnement avaient été réalisés auparavant en raison du faible nombre de composés silicés connus et disponibles commercialement. Mon travail de thèse apporte donc de nouvelles données très importantes sur la connaissance des molécules silicées dans les produits pétroliers.

La dernière partie de ce manuscrit s'intéressera donc à la stratégie analytique qu'il faut mettre en place pour obtenir une spéciation du silicium qui soit représentative des échantillons analysés. Ce travail fera l'objet d'une future publication et est actuellement en cours de préparation. La représentativité des échantillons apparait désormais cruciale pour déterminer les molécules silicées réellement présentes dans les différentes coupes pétrolières issues du raffinage au moment de l'empoisonnement.

Partie D. Apport de la spéciation du silicium pour l'industrie pétrolière

Chapitre 8. A primer in silicon speciation using a complete analytical strategy for the future improvement of catalyst life cycle

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8.1 Abstract

Silicon and its chemical species are of particular interest in petroleum products due to severe poisoning effect of this element on hydrotreatment (HDT) catalysts. The knowledge on silicon speciation was relatively scarce in petroleum products before this work and showed the need to perform speciation studies. In this work, we give several precautions in order to minimize potential problems of contamination occurring during the whole analytical process. A complementary approach between the production of samples representative of PDMS degradation under refining and the development of a novel analytical strategy was proposed. GC/MS SIM was performed for known silicon compounds. For unknown silicon species, ESI-FT-ICR/MS provided the raw formula and DBE of these molecules. However, the determination of the chemical structure was not achievable due to the number of possible isomers. To overcome this challenge, GC-ICP/MS provided the retention times of silicon species and GC/TOFMS giving access to the mass spectrum. Combining FT-ICR/MS results (raw formula and DBE), mass spectrum obtained by GC/TOFMS and fragmentation patterns using MS^n, the chemical structure of silicon compounds was determined. This approach allowed the characterization of more than one hundred silicon species belonging to ten different families in PDMS degradation samples. The presence of silicon was demonstrated for the first time through all petroleum cuts, from the gas fraction (C_1-C_4 cuts) to the heavy oil cuts, according to different degree of polymerization of silicon compounds. Cyclic siloxanes, linear polysiloxanes and ω-dihydroxy polydimethylsiloxanes were confirmed as PDMS thermal degradation products already characterized but with a highest degree of polymerization than previously observed in the literature and under thermal cracking of hydrocarbons. Except for cyclic siloxanes (D_n) that were the major PDMS degradation

products (around 95%), the formation of other silicon species observed at trace levels was clearly dependent on the operating conditions of the process. Under evaluated conditions of steam cracking process, α,ω-dihydroxy polydimethylsiloxanes, methylhydroxycyclic siloxanes, bis(cyclosiloxanyl)siloxane and α-hydroxy,ω-methyl polysiloxanes were mainly formed. Under evaluated coking or visbreaking conditions, volatile silanes, dimethoxy polysiloxanes, hydroperoxy cyclic siloxane, methyl(hydroxyethyl) cyclic siloxanes, linear polysiloxanes and methylpropyl cyclic siloxanes were preferentially produced. Reactive groups containing silicon molecules such as hydroxy, methoxy and hydroperoxy could react with the alumina support of HDT catalysts and lead to the deactivation. Moreover, the structural characterization of several of these silicon species was obtained in naphtha and gasolines where silicon poisoning is a major concern. These results confirmed the dependence of the process on the formation of these silicon species and the representativity of PDMS degradation samples regarding the conditions taking place in real refining processes.

8.2 Introduction

Silicon was known to be a severe poison for HDT catalyst [2, 43] and especially for HDT catalysts processing in the naphtha and gasoline cuts [4]. The deactivation of the catalyst leading to its untimely replacement induced a great economic loss for the oil and gas industry [4, 14]. The understanding of silicon poisoning to increase the life cycle of the catalyst was a very hard task to achieve. In fact, literature review on poisoning reported that silicon species can have a very different effect on catalyst depending on the composition of the catalyst [32], on the experimental conditions [45] but especially on the chemical nature of the silicon molecule [45]. More recently, Tran *et al.* [4] have tried to trap silicon species before the catalytic unit but this system was not successfully operated. Without knowing the chemical structure of silicon species present in petroleum products, it is impossible to optimize a trapping system for silicon compounds. To overcome this challenge, silicon speciation studies must be carried out in petroleum products to identify and quantify the different chemical forms of silicon responsible of catalyst poisoning.

The presence of silicon in petroleum products originates from the use of polydimethylsiloxanes (PDMS) during the oil recovery and as antifoaming to avoid emulsion phenomena in different processes such as distillation, coking, visbreaking, or steam cracking [5, 30]. Under thermal cracking of hydrocarbons, generally operated at 500°C or above, PDMS degrades around 300°C despite its rather good thermal stability [10]. Several authors

[8-11, 13, 34] have studied the thermal degradation of PDMS under inert gas. Cyclic siloxanes (D_n) were identified as the major degradation products of PDMS with some trace of linear polysiloxanes [11]. Moreover, α,ω-dihydroxy polydimethylsiloxanes, known as reactive silicon compounds, can be formed under environmental conditions of degradation by PDMS hydrolysis [110, 306]. However, under refining conditions, no study was yet reported. The severe conditions applied in refining processes could influence the chemical nature of silicon species present in petroleum products. Moreover, several reactions between PDMS degradation products and hydrocarbon radicals could occur and produced very different unknown silicon species. The representativity of the analysed petroleum products samples appeared as a major concern.

In the oil and gas industry, only total silicon concentration was measured by inductively coupled plasma optic emission spectroscopy (ICP-OES) [42] or by inductively coupled plasma mass spectrometry (ICP/MS) [254] but no information about the chemical structure was obtained. Trace level concentrations were ranging from several hundred µg.kg^{-1} to some several mg.kg^{-1} in petroleum products [14]. Regarding speciation studies, the formation of reactive PDMS degradation products, such as α,ω-dihydroxy polydimethylsiloxanes and other unknown silicon species were suspected. To minimize the possible evolution of silicon species between the on-site sampling and the analysis in the lab and to determine the chemical structure of silicon species, the production of representative samples and their analysis using a novel analytical strategy were necessary.

In this work, we present the complementary approach between the production of fresh and representative samples of PDMS degradation under refining conditions and a complete analytical strategy to obtain a representative silicon speciation. The aim was to chase "real" silicon species coming from the thermal degradation of PDMS under refining conditions and potentially responsible of catalyst poisoning. The first part presents a small review focusing on silicon speciation studies reported in petroleum products before this work. A particular attention is paid on potential problems of contamination occurring during silicon analysis and several recommendations were proposed. Several hyphenated techniques and high resolution mass spectrometry were performed to build the analytical strategy applied to silicon speciation and were fully described following their advantages and disadvantages. These different techniques were previously developed and validated in real samples of naphtha or gasoline samples [18, 279, 287, 297]. However, to achieve a representative silicon speciation, PDMS degradation samples under thermal cracking of hydrocarbons, produced using a pilot plant [286], were characterized by the analytical strategy. All silicon species characterized in PDMS degradation samples and in real samples coming from different processes of refinery were presented following their conditions of formation, reactivity and occurrence through the petroleum cuts.

8.3 State of the Art in silicon speciation

8.3.1 Silicon speciation in the oil and gas industry

Before this work, the knowledge of silicon speciation was relatively scarce and especially in petroleum products [14]. Varaprath *et al.* [85] and Chainet *et al.* [14] have published reviews respectively on silicone analysis and its artifacts in 2006 an on silicon speciation by hyphenated techniques in 2011. Most of silicon speciation studies were achieved on commercially available silicon compounds such as cyclic and linear siloxanes using gas chromatography coupled to mass spectrometry (GC/MS) in single ion monitoring (SIM) mode [14, 85].

In the oil and gas industry, no real silicon speciation study was yet reported. Table 8-1 illustrates different works carried out in the oil and gas industry to demonstrate the need to achieve experiments focusing on silicon speciation. The samples and molecules of interest are described with the different advantages and disadvantages provided by each technique. Octamethylcyclotetrasiloxane (D_4) was identified in unleaded gasoline by ^{29}Si NMR (nuclear magnetic resonance) but the sensitivity of this technique was clearly insufficient to determine silicon species at trace levels [70]. More recently, Pohl *et al.* [303] have characterized crude oil residues using micro size exclusion chromatography coupled to inductively coupled plasma high resolution mass spectrometry (µSEC-ICP/HRMS) to determine the molecular distribution of several elements including silicon thanks to the specific and sensitive detection of the ICP/MS. Silicon polymer was highlighted, probably as polydimethylsiloxane, but no information about the molecular characterization can be obtained. High performance liquid chromatography (HPLC) hyphenated to ICP/HRMS was applied to the analysis of silicon compounds commercially available in xylene. This approach could allow the determination of new silicon compounds by their retention time due to specific detection [254]. However, the molecular characterization was only possible for compounds commercially available. In fact, the optimization of the method in xylene was not complete. Several silicon compounds were not totally eluted and the HPLC resolution was not sufficient to separate volatile silicon compounds. Thus, this method cannot be applied to silicon speciation in complex matrices such as petroleum products.

This section clearly demonstrates the need to develop hyphenated techniques to achieve silicon speciation in petroleum products in order to identify silicon species potentially responsible of the deactivation of the catalysts. As previously reported in Varaprath *et al.* [85] and in more details in Chainet *et al.* [14], trace level concentrations and possible contamination problems occurring during silicone analysis have considerably hampered the development of silicon speciation studies. Moreover, the complexity of petroleum products relative to the number of high concentrated hydrocarbons associated to the poor number of silicon standards commercially available strengthened the analytical challenge of this work.

Table 8-1. Previous works achieved for silicon speciation in petroleum products

Techniques	Samples	Molecules	Advantages	Disadvantages	Refs.
^{29}Si NMR	Unleaded gasoline	D_4	Structural characterization	Not adapted for trace concentration	[70]
µSEC-ICP/HRMS	Crude oil residues	Silicon polymers	-Molecular distribution -Specific and sensitive detection	No information about the molecular characterization	[303]
HPLC-ICP/HRMS	Xylene	Silicon standards	Specific and sensitive detection	-Pure silicon standard compounds not completely eluted -HPLC method not adapted to trace level speciation in complex matrix	[254]

8.3.2 Contamination problems during silicone analysis and adapted solutions

The main contamination problems generally occurring during silicon analysis were previously reported in Chainet *et al.* [14] in 2011. The aim of this section is to propose several adapted solutions to minimize these contamination problems and artefacts in order to achieve a representative speciation of silicon. Figure 8-1 illustrates the main contamination problems occurring during silicon analysis and proposes different adapted solutions to minimize these contamination problems in order to achieve a representative speciation [14].

The main observed contamination problems concerned the use of septa in silicones respectively used for vial cap and GC inlet. The degradation of septa caused the formation of cyclic siloxanes (D_n) which are known to be the main compounds of interest in silicon speciation (Figure 8-1) [14]. To reduce these problems, several authors recommended the use of vial cap septa made of teflon (PTFE) [18, 201, 205]. The complementary use of a Merlin microseal septum (Merlin Instrument Company, Half Moon Bay, CA, United States) in replacement of the GC inlet suppressed the formation of cyclic siloxanes as interfering compounds during samples analysis (Figure 8-1). Storage and conservation play an important role during trace analysis. Silicon materials, such as PDMS, have a great affinity for glass and are often adsorbed on the surface [86]. Thus, it is more safety to keep them at lower temperatures in PTFE or plastic containers (preferentially high density polyethylene) [90] (Figure 8-1). This precaution is particularly true for silanols that condense and siloxanes that react in the presence of alkaline surface, acids or strong bases [86]. The important use of silicon species in a wide variety of applications (cosmetics, personal care products and consumer goods) could increase the potential contamination in the lab environment. Thus, extreme care must be taken to avoid the use of these products during silicone analysis. The GC column could be also a source of pollution due to the bleeding of the phase, generally made of PDMS [82, 120]. In fact, the column could release cyclic siloxanes at very low trace level concentrations but the quantity was minor compared to the potential release originating from the septum [14]. However, the use of MS column with a low bleeding allowed to minimize possible trace of siloxanes [14]. Finally, the lubricants, potentially used in the labs for different elements also appeared as a source of pollution but with a minor impact (Figure 8-1).

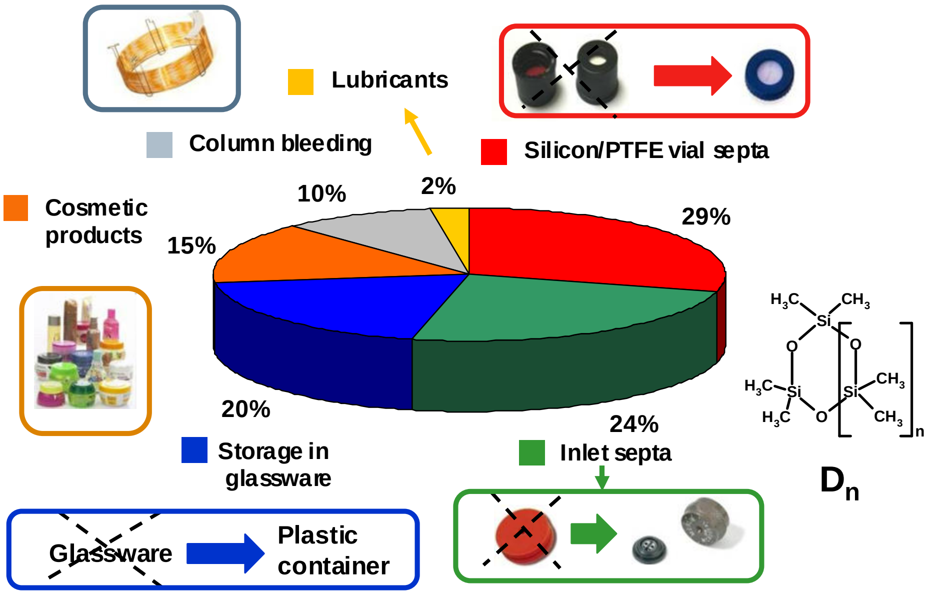


Figure 8-1. Relative estimation of silicon contamination based on literature publications in percent and proposed solutions to minimize these problems (Adapted from Chainet *et al.* [14])

8.4 A complementary approach for silicon speciation

To achieve a representative silicon speciation, a complementary approach between the production of PDMS degradation samples under evaluated conditions of refining using a pilot plant and a novel analytical strategy was presented.

8.4.1 Production of "fresh" and representative samples

Previous works using GC/MS SIM [18] and ESI-FT-ICR/MS [279] in real naphtha and gasolines samples allowed the characterization of several silicon species at trace levels. However, the determination of the chemical structure of silicon species not commercially available was not achievable. Moreover, these results did not give access to a representative speciation due to the possible evolution of silicon species between the on-site sampling and the analysis in the lab without an appropriate storage.

To overcome this challenge, "fresh" and representative samples of PDMS degradation under thermal cracking of hydrocarbons (heptane and xylene as initial source of hydrocarbons) at 500°C were produced using a pilot plant [286]. The concentration of silicon in these samples were higher than in real samples and the complexity of the matrix was also reduced (heptane/xylene) to facilitate the structural characterization of silicon compounds [287]. More details about the production of these samples and the complete analytical strategy (sampling, storage and analysis) were available in Chainet *et al.* [286, 309, 313]. Figure 8-2 presents the different operating conditions, separation steps and the different target silicon compounds formed during PDMS degradation and potentially responsible of catalyst poisoning. PDMS degradation products are classified in three families: volatile silicon compounds, low molecular mass (LMW) silicon compounds and high molecular mass (HMW) silicon compounds. In fact, the application of various analytical techniques will be dependent on this classification and will be described in the next section.

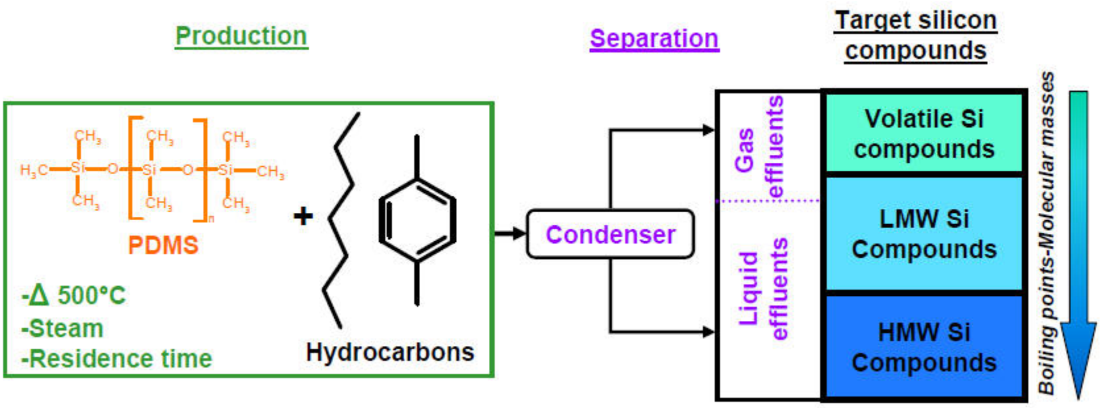


Figure 8-2. Scheme of the production of representative PDMS degradation samples, separation steps and expected target silicon compounds

8.4.2 A novel analytical strategy for silicon speciation

This novel analytical strategy was based on the combination of different hyphenated techniques, mainly including gas chromatography coupled to mass spectrometry and high resolution mass spectrometry. Figure 8-3 illustrates the flow chart of the whole analytical process developed for silicon speciation studies in the oil and gas industry. The scheme was divided in three classes of silicon compounds potentially present in different analyzed samples: volatile silicon compounds, LMW silicon compounds and HMW silicon compounds

Volatile silicon compounds were mainly present in gas fractions and also in naphtha and gasoline samples. To characterize this type of compounds, gas chromatography coupled to time of flight mass spectrometry (GC/TOFMS) equipped with a cryogenic valve was used (Figure 8-3) [309]. Thanks to their retention time and mass spectrum, volatile silicon compounds could be identified by their chemical structure. This identification can be strengthened by the analysis of commercially available silicon molecule. Further details about the LT-GC/TOFMS method were available in Chainet *et al.* [309].

LMW silicon compounds were known to particularly affect HDT catalysts. Due to their boiling points, they were mainly recovered in naphtha and gasoline cuts where severe poisoning by silicon was observed [3, 4]. The characterization of these compounds was a very hard task to achieve because of the wide possible chemical forms. Very different techniques are necessary to obtain their structural information. Two different classes of LMW compounds are defined: known compounds and unknown compounds (Figure 8-3). The step I describe the analysis of known silicon compounds defined as molecules commercially available or previously characterized by their mass spectra. According to the literature, GC/MS SIM (A) was the most employed technique for silicon speciation thanks to its selective and sensitive detection [14, 90] (Figure 8-3). This technique was used to identify and quantify known silicon compounds by their retention times and specific ions [18]. The total silicon content measured by elementary analysis (ICP-OES (AA) or ICP/MS) can be compared to the sum of all silicon species concentrations obtained by GC/MS SIM. If the total silicon content is similar, silicon speciation was obtained. In our case, the total silicon content measured in naphtha and gasoline samples originated from a steam cracking process did not match and the presence of unknown silicon species was suspected [18]. Without knowing their mass spectra and so their characteristic ions, GC/MS SIM cannot be performed to determine silicon species never characterized before.

To characterize unknown silicon compounds defined as silicon species never characterized before (Figure 8-3-step II-i), FT-ICR/MS (B) with an electrospray ionization (ESI) was developed to access to the raw formula and double bond equivalent (DBE) of silicon compounds. [279]. Using electrospray ionization, all silicon compounds with a protonable group could be ionized and detected with high sensitivity. However, the consequent number of possible isomers for each raw formula did not allow to obtain the structural identification of these new silicon species.

For the determination of the chemical structure of unknown molecules, a complementary approach between gas chromatography coupled to inductively coupled plasma mass spectrometry (GC-ICP/MS) (C) and gas chromatography or heart-cutting gas chromatography hyphenated to time of flight mass spectrometry ((GC/TOFMS) (D) or (GC-GC/TOFMS) (E)) was developed. GC-ICP/MS (C) using a dynamic reaction cell (DRC) with hydrogen gas to resolve the interferences ($^{14}N^{14}N^{+}$ and $^{12}C^{16}O^{+}$) on the m/z 28 for silicon provided the retention times of all silicon species present in the samples [297] (Figure 8-3). However, the identification was only based on the atomic signature of the ICP/MS and on the retention time of the analytical standard. The retention times previously determined using GC-ICP/MS were calibrated using retention indices to obtain a same value of retention for each molecule in order to facilitate the recognition of the molecules using different hyphenated techniques [287, 313]. Using these retention indices, GC/TOFMS (D) (Figure 8-3) was carried out to obtain the mass spectrum of silicon compounds [287]. However, due to the relative complexity of the matrix, several silicon compounds were coeluted and their identification cannot be obtained (Figure 8-3) [313]. Contrary to GC-ICP/MS, the TOFMS detection was not specific for silicon and the adding of a dimension of separation was necessary to increase the resolution. To overcome these coelutions, GC-GC/TOFMS (E) was performed [287] (Figure 8-3). The coeluted fraction containing the silicon compound observed in GC/TOFMS was transferred to the second dimension of separation with a different selectivity to successfully resolve the coelutions and give access to the mass spectrum of pure compounds [313]. The GC separation associated to TOFMS detection both in EI (electron ionization) and in CI (chemical ionization) respectively provided information about the fragmentation of the molecule and the molecular mass of the compound. However, the observation of the protonated molecule is dependent on the efficiency of the CI and on the fragility of the silicon molecules [313]. In some cases, the MH^+ peak can not be obtained and the (M-15) peak, relative to the elimination of CH_4 was mostly detected [313]. According to a comparison of the mass spectra with the library, no plausible chemical structure can be obtained for silicon compounds (Figure 8-3-step II-ii). The lack of silicon compounds commercially available associated to the poor number of silicon species mass spectra in the MS library clearly showed the need to combined FT-ICR/MS with GC/TOFMS or GC-GC/TOFMS results. Only a multi-technical approach was adapted to characterize silicon compounds never reported in petroleum products (Figure 8-3). Using raw formula and double bond equivalent (DBE) determined by ESI-FT-ICR/MS (B) and EI and CI mass spectra provided by GC/TOFMS or GC-GC/TOFMS, the chemical structure could be proposed and strengthened by MS^n (F) if the sensitivity was sufficient (Figure 8-3-step II-iii) [313].

HMW silicon compounds referred to silicon molecules with a wide range of molecular masses such as PDMS. These compounds can be come from the partial degradation of the initial antifoaming agent added in feeds [286]. For HMW silicon compounds, µSEC-ICP/HRMS was the most adapted technique. The specific detection of the ICP/HRMS allowed to determine the molecular distribution of PDMS degradation products among the hydrocarbon matrix [286]. µSEC resolution was not sufficient to determine the molecular characterization of individual silicon species but this technique appeared as a powerful analytical tool to macroscopically characterize silicon compounds.

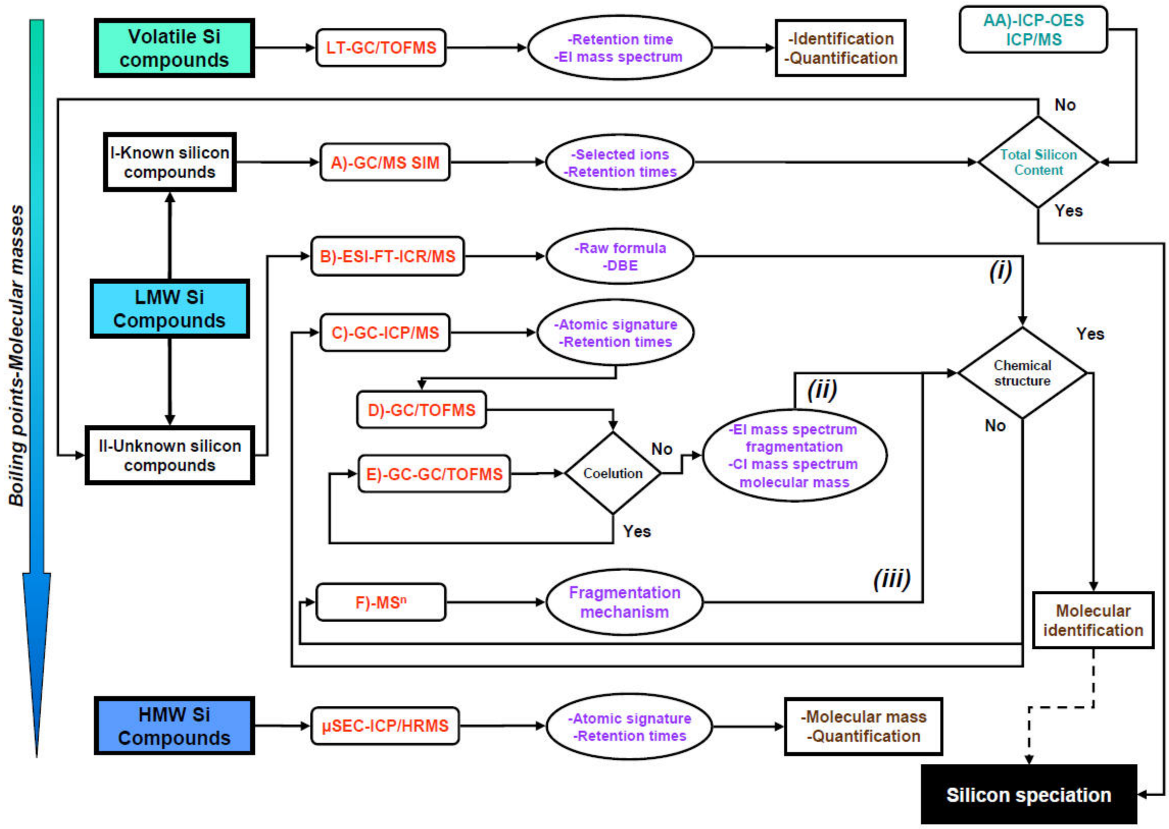


Figure 8-3. Flow chart of the analytical strategy developed for silicon speciation

8.5 Characterization of silicon species through all petroleum cuts

To achieve a representative silicon speciation, PDMS degradation samples produced under thermal cracking of hydrocarbons at 500°C on a pilot plant were carefully stored and analysed using the analytical strategy previously described. This approach clearly allowed the minimization of the possible evolution of silicon species in order to chase the real silicon species present during the poisoning step.

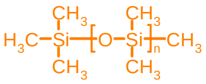
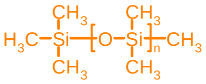
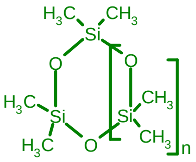
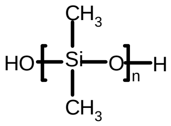
In these samples, more than 100 silicon species were highlighted and belonged to ten different families [309, 313]. Several PDMS degradation products already reported were confirmed in this work (Table 8-2) but a wide array of new silicon species issued from PDMS degradation samples under thermal cracking of hydrocarbons were characterized for the first time (Table 8-3). All these compounds are discussed following their different conditions of formation and their presence in real samples previously analysed. The characterization in real samples was only achievable thanks to the analysis of PDMS degradation samples at higher silicon concentration.

According to their estimated boiling points, these silicon compounds will distillate in the different petroleum cuts from the C_1-C_4 cuts to heavy oils (Figure 8-4) and will be able to affect the performance of the catalysts. The boiling points were estimated based on the boiling points of known compounds (D_n, L_n, trimethylsilanol, dimethoxydimethylsilane).

8.5.1 Known silicon compounds

PDMS thermal degradation was largely studied under inert gas [8-13, 34]. It was established that the thermal degradation process occurred by a depolymerization mechanism and led to the formation of residual linear polydimethylsiloxanes and cyclic siloxanes (D_n). α,ω-dihydroxy polydimethylsiloxanes were also formed by the PDMS hydrolysis [306] or during the thermal degradation of two hydroxy polydimethylsiloxanes [12, 13].

Table 8-2. Known silicon compounds characterized in PDMS degradation samples and in real samples with their conditions of formation

Molecules	Chemical Structure	Conditions of Formation	Real samples
Residual linear polydimethylsiloxanes (40<n>1500)	 $H_3C-Si(CH_3)_2-[O-Si(CH_3)_2]_n-CH_3$	-Initial PDMS was not completely degraded under short residence time -Depolymerization mechanism [10]	[286] Crude oil [303]
-Linear polydimethylsiloxanes (L_2-L_5)	 $H_3C-Si(CH_3)_2-[O-Si(CH_3)_2]_n-CH_3$	-Preferentially formed for long residence time and especially without steam (evaluated coking/visbreaking conditions) -Depolymerization mechanism [10]	L_2, L_3 and L_4 [18, 287]
Cyclic siloxanes (D_3-D_{40})		-All operating conditions -Depolymerization mechanism [10]	D_3-D_6 [18, 279, 287]
α,ω-dihydroxy polydimethylsiloxanes (Si_2-Si_{14})	 $HO-[Si(CH_3)_2-O]_n-H$	-Preferentially formed with steam -PDMS Hydrolysis [306]	n.c.

n.c. never characterized in real samples

In PDMS degradation samples, residual linear polydimethylsiloxanes were characterized with an approximate polymerization degree ranging from 40 to 1500 using µSEC-ICP/HRMS [286]. The initial PDMS was not completely degraded under short residence time at 500°C (Table 8-2). Due to this high degree of polymerization, PDMS could distillate in heavy oil cuts (Figure 8-4) and confirmed the previous hypothesis of Pohl *et al.* [303] using µSEC-ICP/HRMS concerning the detection of PDMS in crude oil. Concerning the naphtha and gasoline cuts, short linear polydimethylsiloxanes (L_2-L_5) were also characterized at trace levels in PDMS degradation samples and especially under long residence time without steam. These molecules were also detected in real naptha and gasolines coming from coking and steam cracking processes (Table 8-2) [18, 287]. Among these compounds, hexamethyldisiloxane (L_2) was known to be a very severe poison for Pt/Al_2O_3 catalyst used in biogas plants for volatile organic compounds (VOC) oxidation and could affect the performance of HDT catalysts in the oil and gas industry.

As previously mentioned, cyclic siloxanes were the major PDMS degradation products (around 95%) under thermal cracking of hydrocarbons recovered but no poisoning effect has been yet reported for these molecules [313]. Cyclic siloxanes ranging from D_3 to D_6 were the main compounds identified in naptha and gasoline coming from different refinery processes [18, 279, 287]. D_3 was the most abundant cyclic siloxane because it was the more thermodynamically stable at 500°C [301]. The relative amount of cyclic siloxanes decreased with the increase of their polymerization degree [14, 313]. Camino *et al.* [11] and Lewicki *et al.* [12] have respectively highlighted cyclic siloxanes up to D_{13} and up to D_{23}. Under our conditions, D_n up to D_{40} were characterized using ESI-FT-ICR/MS and will distillate in higher petroleum cuts than in naphtha and gasoline [313]. These results confirmed Tran *et al*. works, which supposed that the majority of silicon were present in the naphtha range through cyclic form but our work clearly demonstrated that all petroleum cuts were concerned by silicon. No significant differences were observed on the relative abundance of D_n following the different tests up to D_9. The relative amount of cyclic siloxanes above D_9 obtained by GC/MS SIM was more important for PDMS degradation tests under short residence time with steam. This result confirmed that PDMS was less degraded under these conditions as shown using µSEC-ICP/HRMS [286].

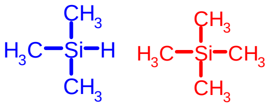
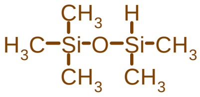
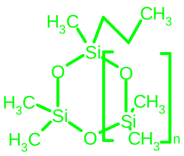
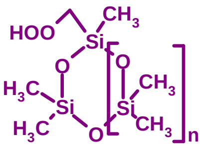
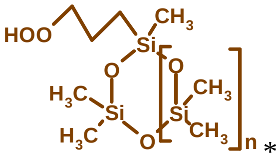
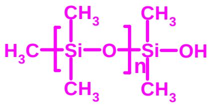
α,ω-dihydroxy polydimethylsiloxanes were characterized in all PDMS degradation samples even if steam was not initially injected (Table 8-2) [313]. These compounds were formed by the hydrolysis of PDMS [110, 306]. Several ppm of water were sufficient for the hydrolysis of PDMS and can explain the formation of α,ω-dihydroxy polydimethylsiloxanes in the absence of steam due to the initial concentration of water in heptane and xylene solvents used as initial source of hydrocarbons [313]. α,ω-dihydroxy polydimethylsiloxanes up to trimer were characterized for PDMS degradation under environmental conditions with very long residence times around several months [110]. In our works, these species were highlighted from Si_2 to Si_{14} and also confirmed the presence of silicon through its chemical structure from naphtha or gasoline cuts to heavy oils. α,ω-dihydroxy polydimethylsiloxanes were never characterized in real petroleum samples, probably due to their possible condensation which led to the formation of linear or cyclic siloxanes [302, 309]. This result demonstrated the importance of the storage and rapid analysis following sampling to achieve a representative speciation of silicon. α,ω-dihydroxy polydimethylsiloxanes were never characterized as poison but the hydroxy group can condense with OH groups of the alumina support catalyst used in HDT and induce the formation of modified silica structure at the surface of the catalysts [50]. The presence of silica can modified the acid properties of the catalyst and affect the catalyst activity and selectivity during HDT [314]. The modification of the catalyst properties can involve its deactivation and its untimely replacement [50].

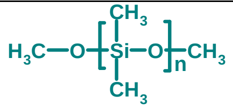
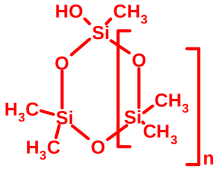
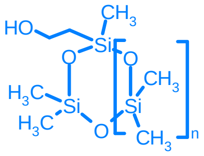
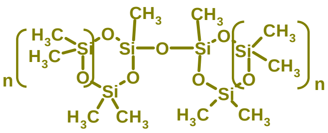
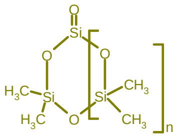
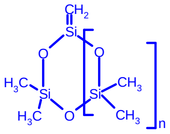
The highlight of these PDMS degradation products already characterized confirmed the previous works reported in the literature and provided further information about these compounds especially concerning their degree of polymerization and their formation under thermal cracking of hydrocarbons. Silicon is present in all petroleum cuts through several chemical forms. Cyclic siloxanes (D_n) are the major silicon compounds but a wide array of other silicon species at lower concentration levels (<5% of all silicon species), almost never characterized before, are also present and will be further discussed in the next section.

8.5.2 New PDMS degradation species under thermal cracking of hydrocarbons

The wide array of these new silicon compounds is presented in details in Table 8-3 to describe the conditions of formation and their detection in real samples previously analysed. They are also displayed in function of their estimated boiling points according to the different petroleum cuts in Figure 8-4. This representation clearly shows that all petroleum cuts (from gas fractions to heavy oil cuts as indicated in Table 8-3 are concerned by the presence of these new molecules, as previously reported for the known silicon compounds.

Table 8-3. New silicon compounds characterized in PDMS degradation samples and in real samples with their conditions of formation.

Molecules	Chemical Structure	Conditions of Formation	Real samples
Silanes Trimethylsilane Tetramethylsilane		-Formed for long residence time and especially without steam (evaluated coking/visbreaking conditions) -Formation by Si-CH_3 scission of PDMS [10]	n.c.
Pentamethylsiloxane		-Evaluated coking/visbreaking conditions -Formation by a depolymerization mechanism [10]	n.c.
Methylpropyl cyclic siloxanes (Si_3-Si_5)		Possible reaction of PDMS degradation product with carbon radicals [313]	n.c.
Methyl(methylhydroperoxy) cyclic siloxane (Si_3-Si_6)		- Evaluated coking/visbreaking conditions -Formation by the occurrence of side-chain peroxides [10, 301] -Si_4 compound identified during the reaction of D_4 with $OH^\bullet$ [107]	Si_4-Si_5 [297]
Methyl(propylhydroperoxy) cyclic siloxane (Si_3-Si_6)			Si_4 [297]
α-hydroxy,ω-methyl polysiloxanes (Si_1-Si_8)		-Evaluated coking/visbreaking conditions -Reaction of L_n with $OH^\bullet$ [312]	Si_1 [297]

Molecules	Chemical Structure	Conditions of Formation	Real samples
Dimethoxy polysiloxanes (Si_1-Si_8)		Evaluated coking/visbreaking conditions	Si_2 [279]
Hydroxymethyl cyclic siloxanes (Si_3-Si_9)		-All operating conditions -Reaction of D_4 with $OH^{\bullet}$ [107]	Si_4 [297]
Methyl(hydroxyethyl) cyclic siloxanes (Si_3-Si_9)		Evaluated coking/visbreaking conditions	Si_5 [297]
Bis(cyclosiloxanyl)siloxane (Si_6-Si_{10})		-All operating conditions but favoured with steam -This molecule was already characterized during the reaction of D_4 with $OH^{\bullet}$ [107] -Possible cyclisation of two hydroxy methyl cyclic siloxanes [313]	Si_6 [297]
Cyclic silanones (Si_3-Si_{10})		All operating conditions but preferentially formed with steam and especially for short residence time	Si_4 [297]
Silene cyclic siloxanes (Si_3-Si_{10})		All operating conditions but mainly formed with steam	Si_5-Si_6 [279]

n.c. never characterized in real samples

Silanes such as trimethylsilane and tetramethylsilane were identified for the first time in the gas fraction of PDMS degradation samples [309]. Silanes were formed under long residence times and especially without steam (evaluated coking or visbreaking conditions). These molecules could be formed by the scission of the Si-CH_3 bond through radical mechanism [10]. Trimethylsilane and tetramethylsilane (Table 8-3) were suspected as poisons for Pd catalyst during cyclohexene deshydrogenation [57]. The performance of Pd and Pt catalysts used during cyclohexene deshydrogenation was clearly affected by triethylsilane [45, 46]. According to known their boiling points, the characterized silanes could be present in the gas or liquefied petroleum gas (LPG) cuts (C_1-C_4) and potentially explained the poisoning of the light petroleum cuts where severe problems of silicon poisoning were suspected but never demonstrated [43, 307] (Figure 8-4). Under these evaluated of coking or visbreaking conditions, pentamethylsiloxane was also characterized in PDMS degradation samples [309]. This volatile siloxane can be produced by a depolymerization mechanism followed by the rupture of the Si-CH_3 to form a Si-H by a radical mechanism [10] and will be potentially present in the naphtha or gasoline cuts.

Methylpropyl cyclic siloxanes were characterized from Si_3 to Si_5 under long residence time and especially without steam. This type of silicon compounds was never highlighted in real samples, probably due to very low concentration levels observed. The propyl group linked to silicon atom can originate from the reaction between PDMS degradation products and carbon radicals [313]. Due to their polymerization degree (Si_3-Si_5), these molecules could be present from naphtha or gasoline cuts to kerosene cuts. Methyl(methylhydroperoxy) cyclic siloxane and methyl(propylhydroperoxy) cyclic siloxane with approximatively the same degree of polymerization were formed in all degradation conditions but with a high abundance under long residence time and without steam. A mechanism was previously proposed for the formation of these compounds by the occurrence of side-chain peroxides [10]. Heptamethyl(hydroperoxymethyl) cyclotetrasiloxane (Si_4) was also highlighted using GC/MS during the gas phase reaction of octamethylcylcotetrasiloxane (D_4) with hydroxy radicals [107] (Table 8-3). The Si_4 and Si_5 (hydroperoxymethyl) cyclic siloxane and the Si_4 (hydroperoxypropyl) cyclic siloxane were previously detected at trace levels in gasoline and naphtha samples and clearly demonstrated the good representativity of the production of PDMS degradation samples [297] (Table 8-3).

Two new PDMS degradation products with a number of silicon atoms ranging from 1 to 8 were highlighted and could distillate from naphtha or gasoline to diesel cuts (Table 8-3 and Figure 8-4). α-hydroxy,ω-methyl polysiloxanes were characterized in all PDMS degradation tests but are preferentially formed under long residence and without steam [313]. Stewart *et al.* [312] have identified these molecules during the gas phase reaction between linear polysiloxanes (L_n) and hydroxy radicals. The formation of trimethylsilanol (Si_1), mainly characterized in the gas fraction of PDMS degradation samples, was also enhanced during long residence time [309]. TMSOH was also characterized in naptha taking from a steam cracking process using GC-ICP/MS thanks to the specific detection of the ICP/MS [297]. Using MS detection, the selectivity was not sufficient to detect this volatile compound among hydrocarbons present at high concentrations. However, these silanol compounds are generally unstable and tend to condense in acidic or alkaline environments to produce siloxanes [302]. The condensation of TMSOH, leading to the formation of hexamethyldisiloxane (L_2), was observed in the gas fraction analysis and confirmed the need of a careful storage and rapid analysis. The study of the evolution in the liquid fraction was not achieved but further experiments must be performed using GC-ICP/MS.

Dimethoxy polysiloxanes were characterized with the same degree of polymerization during PDMS degradation under thermal cracking of hydrocarbons. These compounds were mainly produced under long residence times and especially without steam (evaluated coking or visbreaking conditions). The Si_2 dimethoxy polysiloxane was previously detected using ESI-FT-ICR/MS in several samples of naphtha and gasoline coming from a steam cracking process [279].

Hydroxymethyl cyclic siloxanes and hydroxyethylmethyl cyclic siloxane were formed with a polymerization degree ranging from 3 to 9 and could be present from naphtha or gasoline cuts to diesel cuts. Hydroxy methyl cyclic siloxanes were characterized in all degradation conditions. Heptamethylhydroxytetracyclosiloxane (Si_4) was previously identified by Sommerlade *et al.* [107] during the gas phase reaction of octamethylcyclotetrasiloxane (D_4) and hydroxy radical in a smog chamber (Table 8-3). This molecule was also previously detected in naphtha sample coming from a steam cracking process [279] and could be formed by the same reaction due to the high concentration of cyclic siloxanes (D_n). The ethylhydroxy cyclic siloxanes were preferentially formed under long residence time and without steam at a lower amount than the methylhydroxy cyclic siloxanes. The Si_5 species was detected using ESI-FT-ICR/MS in naphtha sample coming from a steam cracking process [279]. Moreover, heptamethyl(hydroxymethyl) cyclotetrasiloxane, with one lower CH_2 alkylation, was previously observed by Sommerlade *et al.* [107]. These latter silicon compounds characterized by their chemical structures were observed in all degradation conditions but were preferentially produced in the presence of steam [313]. Bis(cyclosiloxanyl)siloxane could be formed by the condensation of two hydroxy methyl cyclic siloxane previously characterized [313]. This type of molecule was stable for six silicon atoms fitted to the formation of two pentamethylcyclotrisiloxane linked by a Si-O bond (Table 8-3). This Si_6 molecule was characterized in several naphtha and gasoline taking from different refining processes (coking, steam cracking) [297] and also by Sommerlade *et al.* [107] with the Si_4 hydroxy methyl cyclic siloxane. In PDMS degradation samples, Bis(cyclosiloxanyl)siloxane were characterized from Si_6 to Si_{10} and could be present from the naphtha or gasoline cuts to heavy oil cuts depending on their polymerization degree.

Cyclic silanones and silene cyclic siloxanes were characterized in all operating conditions with a polymerization degree ranging from 3 to 10 but preferentially in the presence of steam

(Table 8-3) [313]. However, silanone and silene functions were known to be reactive intermediates and appeared as very unstable [311]. Based on the silicon chemistry, raw formula and DBE, EI mass spectrum and MS^n experiments, these chemical structures were the most possible [313]. These compounds are not represented in Figure 8-4 but could be present from naphtha and gasoline cuts to heavy oil cuts. This type of compounds was never reported in the literature but the Si_4 cyclic silanone was recovered thanks to this work in a gasoline coming from a steam cracking process [297]. The Si_5 and Si_6 silene cyclic siloxanes have been detected in naphtha and gasoline samples coming from steam cracking processes previously analysed using FT-ICR/MS [279].

In this part, we demonstrate that a wide array of silicon species never reported before were characterized at trace levels in PDMS degradation samples and could distillate in all petroleum cuts, from gas fraction to heavy oil cuts. These different silicon species may affect the performance of catalysts present in refining processes. Several new reactive such as hydroxy, methoxy and hydroperoxy groups containing molecules were highlighted. These results appeared as a real advance to progress on the understanding of silicon poisoning. The analytical strategy developed and applied to PDMS degradation samples, produced and carefully stored to minimize the evolution of silicon compounds, was crucial to determine their structural identification. This combination allowed the characterization of these compounds in real samples previously analysed by the different techniques. The presence of silicon compounds both in PDMS degradation samples and in real samples coming from different processes of refinery confirmed the correct representativity of PDMS degradation under refining conditions in this work. Except for cyclic siloxanes, the formation of other silicon species coming from PDMS degradation under thermal cracking of hydrocarbons was clearly dependent on the operating conditions. Their chemical form will be different according to the refining process.

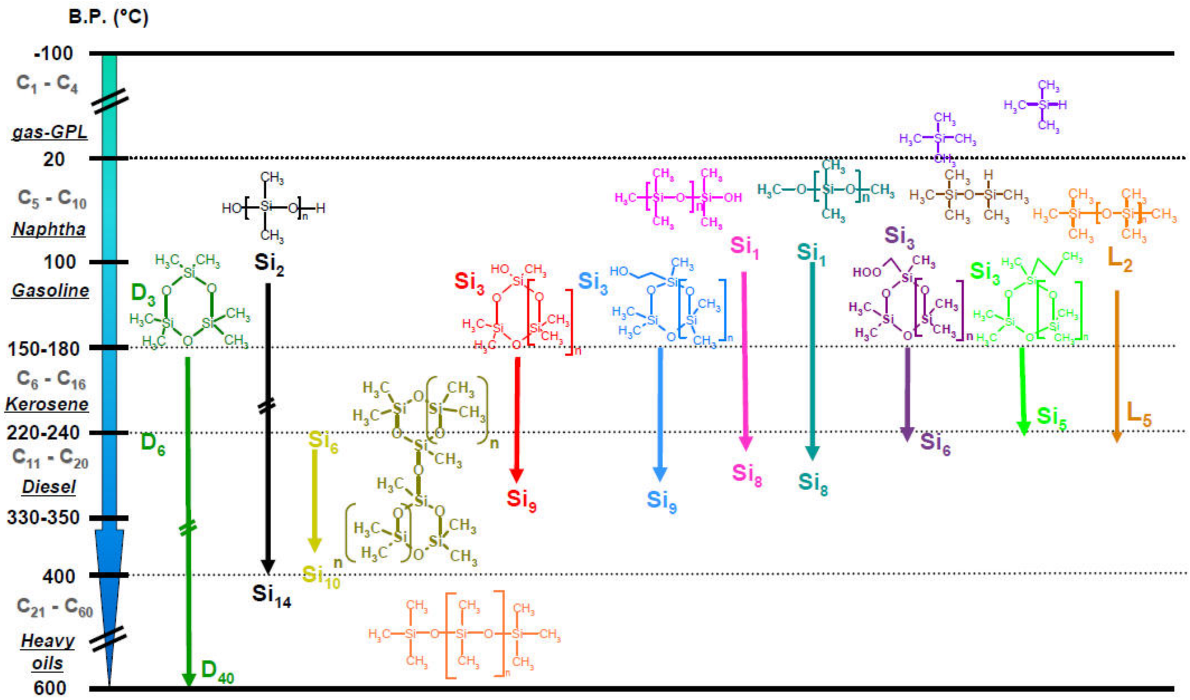


Figure 8-4. Silicon species characterized in PDMS degradation samples produced under thermal cracking of hydrocarbons represented according to their estimated boiling points in the different petroleum cuts

In this part, we demonstrate that a wide array of silicon species were characterized in PDMS degradation samples and could distillate in all petroleum cuts, from the gas fraction to heavy oil cuts. These different silicon species may affect the performance of catalysts present in refining processes. The analytical strategy developed and applied to the PDMS degradation samples, produced and carefully stored to minimize the evolution of silicon compounds, was crucial to determine their structural identification. This combination allowed the characterization of these compounds in real samples previously analyzed by the different techniques. The presence of silicon compounds both in PDMS degradation samples and in real samples coming from different processes of refinery confirmed the correct representativity of PDMS degradation under refining conditions in this work. The formation of silicon species coming from PDMS degradation under thermal cracking of hydrocarbons were clearly dependent on the operating conditions and their chemical form will be different according to the refining process.

8.6 Conclusions

The untimely replacement of hydrotreatment catalysts in the oil and gas industry due to silicon poisoning has clearly demonstrated the need to achieve silicon speciation in petroleum products. Before this work, the knowledge of silicon speciation in petroleum products was relatively scarce. The development of these studies were clearly hampered by the potential problems of pollution during silicone analysis, the poor number of commercially available analytical standards, the presence of silicon at trace levels and the complexity of the matrix.

This work presented the complementary approach between the production of PDMS degradation samples under evaluated conditions of refining using a pilot plant and the analytical strategy developed to obtain a representative silicon speciation. Adapted solutions to minimize the contamination during silicon analysis were also proposed. The application of the analytical strategy using an appropriate storage for PDMS degradation samples allowed the characterization of more than one hundred silicon species which could distillate through the different petroleum cuts from gas to heavy oil cuts.

Cyclic siloxanes, linear polysiloxanes and α,ω-dihydroxy polydimethylsiloxanes were confirmed as PDMS thermal degradation products. The presence of these compounds with a higher degree of polymerization than previously defined in the literature demonstrated the presence of silicon through all petroleum cuts. A wide array of silicon compounds, never characterized before, was especially highlighted in this work. Volatile silanes were identified and could potentially explain the poisoning effect of light petroleum cuts. The condensation of trimethylsilanol to form hexamethyldisiloxane was observed in the gas phase of PDMS degradation samples and clearly demonstrated the importance of the storage and rapid analysis to achieve a representative speciation. Except for cyclic siloxanes characterized at high concentrations, the formation of the other silicon species at trace levels clearly depended on the operating conditions of the refining processes. In the presence of steam (evaluated steam cracking), α,ω-dihydroxy polydimethylsiloxanes, methylhydroxy cyclic siloxanes, bis(cyclosiloxanyl)siloxane and α-hydroxy,ω-methyl polysiloxanes were mainly formed. Under evaluated conditions of coking or visbreaking (absence of steam), dimethoxy polysiloxanes, hydroperoxy cyclic siloxane, methyl (hydroxyethyl) cyclic siloxanes, linear siloxanes and methyl propyl cyclic siloxanes were preferentially produced. Consequently, the chemical structure of silicon species will be different in function of the refining process. This result was confirmed by the characterization of several silicon species in real samples previously analysed coming from different refining processes. The structural identification in real samples was only possible thanks to this speciation in representative PDMS degradation samples.

Regarding naphtha and gasoline cuts where silicon poisoning was the most consequent, GC-ICP/MS appeared as the most adapted solution for silicon speciation thanks its specific detection for silicon. All retention times of silicon species could be obtained and the chemical structure could be determined thanks to their retention indices. For compounds with an unknown indice, their chemical structure will be further investigated using GC-GC/TOFMS. For a molecular characterization of higher cuts such as diesel, analytical methods must be adapted and further developments using comprehensive GCxGC coupled to mass spectrometry must be probably developed. For a macroscopic characterization of silicon in heavy oil cuts, µSEC-ICP/MS was successfully carried out.

This work was a primer in silicon speciation and provided the characterization of a wide array of different silicon species never reported before coming from the thermal degradation of antifoaming under refining conditions. Thanks to the silicon speciation, future innovative solutions to minimize the silicon poisoning on HDT catalysts will be proposed in the oil and gas industry.

Conclusions et Perspectives

L'objectif de mon travail de thèse consistait à **mettre en place un ou plusieurs outils de spéciation du silicium** afin de **déterminer les molécules silicées formées dans les charges d'hydrotraitement** et plus particulièrement au niveau des charges naphtas et essences. Pour relever ce défi, une stratégie multi-technique inédite basée sur des outils analytiques de pointe associée à la production d'échantillons de dégradation du PDMS dans des conditions de craquage thermique d'hydrocarbures a été mise en place.

Dans un premier temps, notre stratégie analytique s'est orientée vers la **GC/MS SIM** pour l'identification et la quantification d'une dizaine de **composés silicés connus dans des essences**. Ce travail constitue la première étude de spéciation du silicium dans le domaine pétrolier. Avec des limites de quantification comprises entre 4 et 190 µg.kg^{-1}, les siloxanes cycliques (D_3-D_6) sont les composés majoritairement retrouvés dans des naphtas et essences issus d'un procédé de vapocraquage. Cependant, la comparaison de la concentration en silicium total mesurée par GC/MS SIM et par ICP-OES a montré que seulement 50% des espèces silicées étaient quantifiées.

La sensibilité de la méthode **ESI-FT-ICR/MS** (80 ng.kg^{-1} <LOD< 5 µg.kg^{-1}) associée à la construction de **diagrammes de Kendrick** s'est avérée très performante pour la **recherche des composés silicés inconnus** appartenant à la même famille que les composés silicés modèles. Plus de 50 nouvelles espèces silicées, appartenant aux familles O_2Si, O_3Si et O_4Si et comportant plusieurs insaturations, ont été caractérisées. Cependant, l'accès à leur structure chimique est limité en raison du nombre conséquent d'isomères pour chaque formule brute obtenue.

Pour progresser vers l'élucidation structurale des composés silicés inconnus, les temps de rétention détectés par GC-ICP/MS ont servi de base pour l'obtention des spectres de masse par GC-GC/TOFMS. Malgré des limites de détection élevées (20 <LOD (µg de Si.kg^{-1}) <140) obtenues par **GC-ICP/MS** et une réponse non universelle pour le silicium, une vingtaine de **composés silicés inconnus** a été détectée dans différents échantillons. Avec des LOD équivalentes à la GC/MS SIM, la **GC-GC/TOFMS** a montré tout son potentiel pour **retrouver les composés silicés** par leurs indices de rétention. Néanmoins, en raison de la complexité des matrices et des concentrations traces retrouvées, l'accès à la structure chimique des composés inconnus s'est avéré très complexe. De plus, les espèces silicées identifiées ne seront pas forcément représentatives de celles initialement formées.

Afin d'être sûr d'identifier les formes chimiques du silicium réellement présentes au moment de l'empoisonnement, la spéciation a été effectuée dans des échantillons représentatifs de la dégradation du PDMS produits sous des conditions de craquage thermique d'un mélange heptane/xylène. L'application de notre stratégie analytique a permis de caractériser structuralement **plus d'une centaine de molécules silicées issues de la dégradation du PDMS** dans des conditions représentatives des procédés de raffinage. Pour la première fois, nous avons démontré la possible **présence du silicium** sous une **multitude de formes chimiques** comprenant un nombre d'atomes de silicium (n) entre 1 et 1500. Autrement dit, ces espèces silicées vont donc pouvoir distiller dans **toutes les coupes pétrolières**, des coupes gaz (C_1-C_4) jusqu'aux coupes les plus lourdes (C_{21}-C_{60}). La plupart de ces espèces a conservé le même motif de répétition C_2H_6OSi, initialement présent dans le PDMS.

Dans un premier temps, **les siloxanes cycliques (D_n)** ont été confirmés comme les **composés majeurs** de dégradation du PDMS. Ils représentent **au moins 95%** de la totalité des composés mise en évidence selon les conditions appliquées. Leur formation est accompagnée de siloxanes linéaires avec différents degrés de polymérisation. Du PDMS non totalement dégradé en présence de vapeur d'eau et pour des temps de séjour courts (conditions de vapocraquage) a été observé ($40<n<1500$). Des α,ω-dihydroxy polydiméthylsiloxanes, en quantités beaucoup plus faibles que les D_n, ont également été caractérisés comme produits d'hydrolyse du PDMS mais avec des degrés de polymérisation supérieurs à ceux observés dans la littérature.

Dans un second temps, nous avons pu mettre en évidence **des composés silicés jamais caractérisés jusqu'à présent** lors de la dégradation du PDMS et dont la formation est très dépendante des conditions des procédés. La spéciation du silicium sera donc différente en fonction de l'origine des échantillons analysés. Ces composés, dont les α,ω-dihydroxy polydiméthylsiloxanes, sont **présents en très faibles quantités** (**5%** de la totalité des composés) mais possèdent **des fonctions de type hydroxy, méthoxy ou hydropéroxy très réactives**. Ces dernières vont pouvoir interagir avec les catalyseurs, notamment ***via* une possible réaction avec le support en alumine du catalyseur**, et conduire à un empoisonnement.

En présence de vapeur d'eau, utilisée dans le **procédé de vapocraquage**, des composés de type, méthylhydroxy siloxanes cycliques et α-hydroxy,ω-méthyl polysiloxanes ont été majoritairement caractérisés. Ces espèces peuvent être respectivement formées par réaction des siloxanes cycliques (D_n) et des polysiloxanes linéaires (L_n) avec des radicaux hydroxy. La condensation de deux méthylhydroxy siloxanes cycliques peut également conduire à la formation de bis(cyclosiloxanyl) siloxane. Au contraire, dans des **conditions de cokéfaction ou de viscoréduction**, la formation de silanes volatils et de composés hydropéroxy siloxanes cycliques par des mécanismes de peroxydation initiés par des radicaux a été observée. Des siloxanes linéaires (L_n) et des diméthoxy polydiméthylsiloxanes se forment également dans ces conditions. Finalement, la présence de méthyl (hydroxyéthyl) siloxanes cycliques et de méthylpropyl siloxanes cycliques laisse penser à une réactivité entre des produits de dégradation du PDMS et des radicaux carbonés.

La **réactivité des composés silicés** a également été mise en évidence par l'observation de la condensation du triméthylsilanol (TMSOH) dans la fraction gazeuse pour former de l'hexaméthyldisiloxane (L_2). Mes résultats de thèse montrent bien **l'importance d'un stockage adapté** et **d'une analyse rapide** pour ces composés afin de minimiser leur possible évolution au cours du temps.

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Malgré tout l'apport de mon travail, des efforts restent à fournir au niveau des développements analytiques pour la caractérisation de charges pétrolières supplémentaires et d'un point de vue catalytique pour améliorer la durée de vie des catalyseurs d'HDT sensibles à l'empoisonnement par le silicium.

D'un point de vue analytique, la GC-ICP/MS apparaît comme la technique de choix pour la spéciation du silicium grâce sa détection spécifique permettant un accès aux temps de rétention des molécules détectées qui sont ensuite convertis en indices. A partir de mon travail de thèse, les molécules désormais connues sont identifiées structuralement. Pour les composés inconnus, l'approche avec la GC-GC/TOFMS reste nécessaire.

Néanmoins, **des développements supplémentaires par GC-ICP/MS** sont indispensables pour abaisser les limites de détection actuelles en utilisant des matériaux autres que le quartz qui relargue potentiellement du silicium dans la torche. De plus, **la quantification** est pour le moment dépendante de calculs de coefficients de réponse et se limite donc aux composés silicés disponibles commercialement. Des progrès sont nécessaires au niveau de la ligne de transfert pour aller vers une réponse universelle du silicium. Par la suite, plusieurs charges de type naphtas et essences provenant de différents procédés pourront être analysées pour disposer d'une cartographie des espèces silicées en fonction des procédés utilisés.

Pour **des charges plus lourdes** et donc plus complexes, contenant du silicium, la **GC-ICP/MS** pourra probablement être appliquée à des coupes gazoles. Néanmoins, la **FT-ICR/MS** et la **GCxGC-HT** couplée à la spectrométrie de masse haute résolution (HRTOFMS) peuvent offrir de bonnes perspectives pour la spéciation du silicium dans des gazoles et également pour l'analyse du silicium dans des coupes plus lourdes tout en s’assurant de la bonne représentativité des échantillons.

Jusqu’à présent, des tests d’empoisonnement avaient été effectués sur des molécules modèles choisies sans connaître les véritables composés présents dans les charges. Cette spéciation du silicium dans des échantillons représentatifs constitue donc un apport considérable pour progresser sur la compréhension de l'empoisonnement des catalyseurs. Connaissant désormais les espèces présentes, **des systèmes de piégeage des molécules silicées** en amont des unités catalytiques vont pouvoir être testés et optimisés afin d’éliminer ces composés indésirables. Le deuxième axe consistera à renforcer la résistance du catalyseur vis-à-vis du silicium pour assurer le maintien de son activité. Pour cela, **des tests d’empoisonnement** ou **des travaux de modélisation** sur les véritables molécules mises en évidence devront être réalisés afin de comprendre les mécanismes d’empoisonnement. La majorité des molécules silicées caractérisées sont non disponibles commercialement et une synthèse de ces composés est probablement indispensable pour progresser dans ces deux axes.

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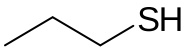
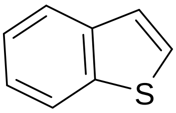
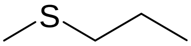
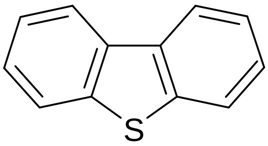
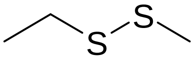
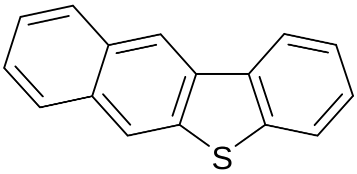
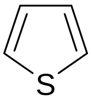
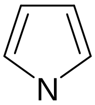
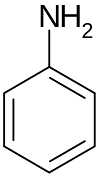
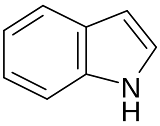
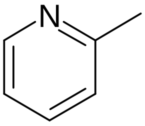
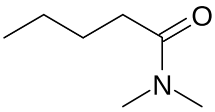
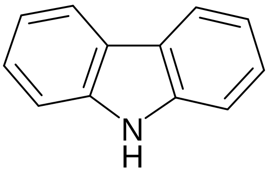
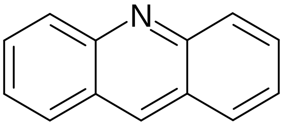
Annexes

Annexe 1 : composés NSO

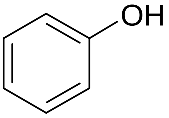
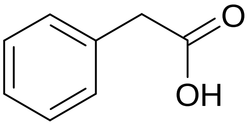
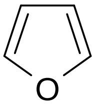
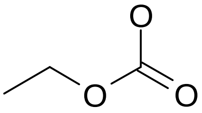
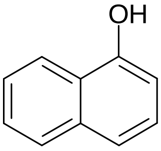
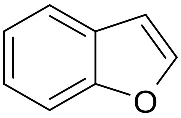
Soufrés

Familles	Exemples	Familles	Exemples
Mercaptans $C_nH_{2n+1}SH$		Benzothiophènes	
Sulfures R-S-R'		Dibenzothiophènes	
Disulfures R-S-S-R'		Naphtodibenzothiophènes	
Thiophènes			

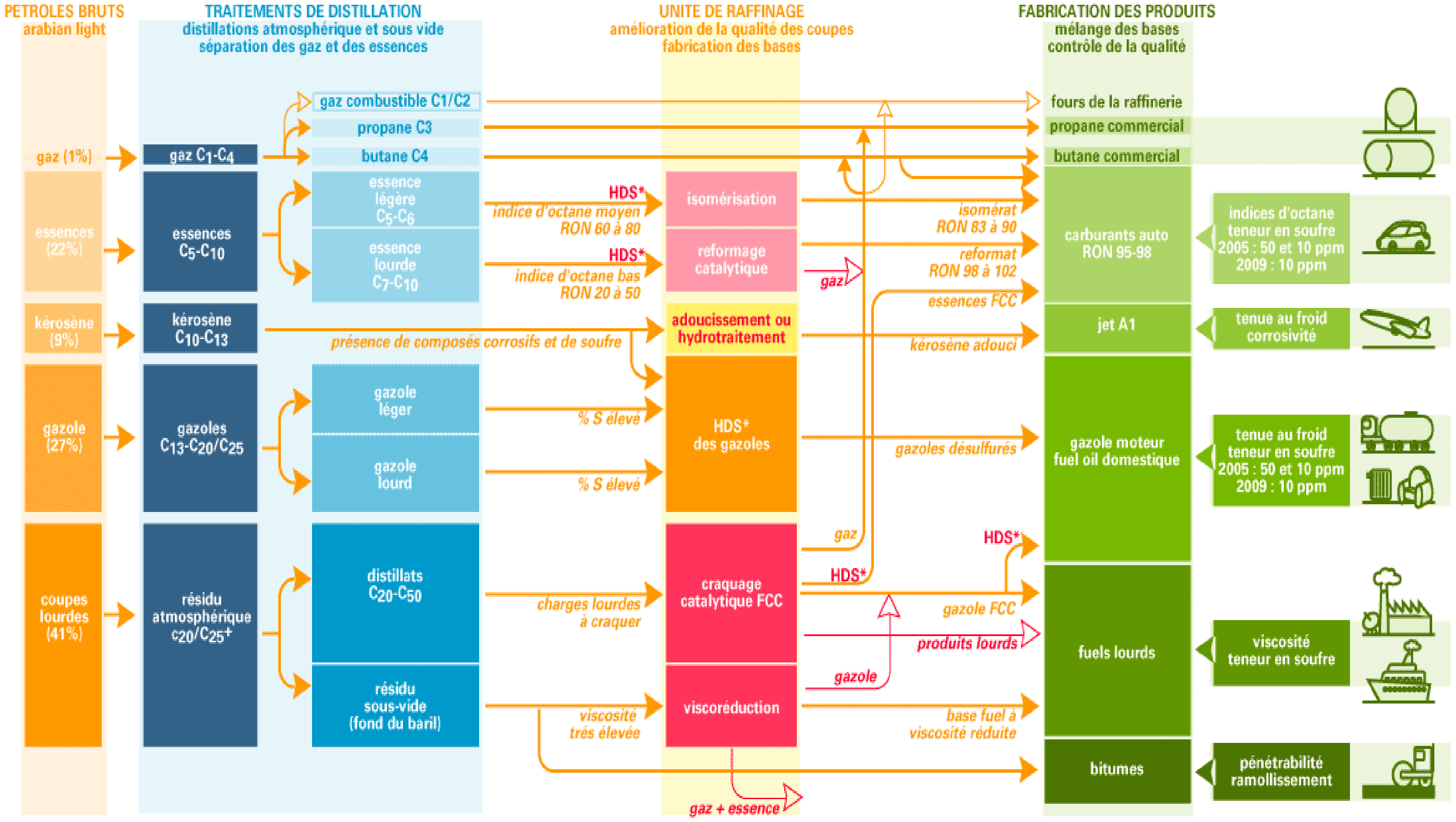
Azotés

Composés neutres		Composés basiques	
Familles	Exemples	Familles	Exemples
Pyrroles		Aniline	
Indoles		Pyridine	
Amides			
Carbazoles		Acridine	

Oxygénés

Familles	Exemples	Familles	Exemples
Phénols		Acides Naphténiques	
Furanes		Esters	
Naphtol		Benzofurane	

Annexe 2 : Schéma de principe du Raffinage



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HDS* : hydrodésulfuration : élimination du soufre par l'hydrogène

Annexe 3 : Procédés du raffinage

Famille de procédés	Mécanismes	Noms	Charges	But	Conditions	Produits
Amélioration des propriétés	Réarrangement moléculaire	Réformage catalytique	-Essences lourdes (80-180 °C) -20<RON<50	-Transformer les charges en isoparaffines et aromatiques -Augmenter l'indice d'octane des coupes légères du brut -Produire de l'hydrogène	-Catalyseur -P=2 à 5 bars -T=510-530 °C	-Réformat à haut indice d'octane (RON>100, Aromatiques) -Sous produits : H_2, gaz, GPL pour être hydrotraités
		Isomérisation	Paraffines	-Transformer les paraffines en isoparaffines (60<RON<80) -Augmenter l'indice d'octane	-Basse T -P moyenne -Catalyseur spécifique	Isopentane et C_6 (diméthylbutane)
	Intervention de co-réactifs	Alkylation	-Oléfines légères (C_3-C_5) -Charges du vapocraqueur ou craquage catalytique	Augmenter indice d'octane par ajout d'isobutane	-Réaction exothermique -Catalysée par acides forts	Isoparafines (C_7-C_8)
		Oligomérisation (Dimérisation)	Issues du craquage catalytique	Production d'essence		Essences
Conversion	Voie thermique	Viscoréduction	Résidus atmosphériques et sous vide	Transformer les lourds en produits légers (réduire la viscosité)	-T=450-500 °C -P=5-20 bars	-Coupe C_3-C_4 -Essence vers HDT -Distillat lourd vers HCK -Distillat léger vers HDS -Résidu
		Cokéfaction	Résidus atmosphériques et sous vide	Produire des coupes légères (gaz, essences, gazoles et distillats)	-T=500 °C -Temps de séjour important (24 heures)	-Coupe légère -Production de coke (qualité d'électrode) -Hydrotraitement des produits nécessaire
		Vapocraquage	Fractions légères et lourdes du brut	Produire des oléfines (C_2-C_4) et des aromatiques (BTX)	-Vapeur d'eau -T=800 °C -Temps de séjour très court (0,08-1,2 secondes)	-Éthylène, propène, butadiène, butène et aromatique -Sous produits : H_2, CH_4, fuel résiduel
	Voie catalytique	Craquage catalytique	Distillats sous vide brut ou de conversion	Production d'essences	-T=500-540 °C -Temps de séjour de 1s -Catalyseur silice-alumine	-Essences de bon indice d'octane -Gaz liquéfiés, C_5 et LCO
		Hydrocraquage	Distillats sous vide brut ou de conversion	Production de kérosène et de gazole de qualité	-T=350-400 °C -P=160-180 bars de H_2 -Catalyseur	Essence légère et lourde mais majoritairement du kérosène et gazole

Conversion	Voie catalytique	Hydroconversion	Résidus atmosphériques et sous vide	Convertir partiellement les charges lourdes fortement polluées	-P=150-200 bars de H_2 -Catalyseurs	-Fraction essences -Distillats et résidu -Élimination des impuretés (métaux, asphaltènes)
Finition		Hydrotraitement	Coupes pétrolières	Éliminer les composés indésirables (NSO, métaux, aromatiques...)	-H_2 et catalyseurs -T=320 et 390 °C -P= 20 à 200 bars	Amélioration de la qualité des produits
Protection de l'environnement		Traitement des gaz acides				
		Fumées				
		Eaux de rejet				

Abréviations
BTX : Benzène, Toluène, Xylène
GPL : Gaz de Pétrole Liquéfié
HDS : Hydrodésulfuration
LCO : Light Cycle Oil
NSO : Composés Azotés, Soufrés, Oxygénés
P : Pression
RON : Indice d'Octane Recherche
T : Température

Annexe 4 : Supporting information du chapitre 4

Supporting information-Combining Fourier Transform-Ion Cyclotron Resonance/Mass Spectrometry Analysis and Kendrick Plots for Silicon Speciation and Molecular Characterization in Petroleum Products at Trace Levels

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Table of Contents:

1-Algorithm of the "Get family" function

Introduction

The aim of the function is to search, select and display on Kendrick plots compounds which have different alkylation (CH_2) and different unsaturations (KMD) than a reference molecule. In our case, the function is calibrated with silicon standard compounds previously analyzed by ESI-FT-ICR/MS.

The algorithm was applied to an Excel worksheet containing FT-ICR/MS raw data such as measured masses, intensity, theoretically masses, error (ppm) and elemental composition. All peaks with a signal to noise ratio equal or higher than six times of the standard deviation of the baseline noise were integrated by the software, designed at IFPEN, and automatically calculated the mass spectra and the Kendrick plots.

The algorithm begins with the highest peak intensity. The search is based on the Kendrick mass difference between this reference peak and other detected peaks among the x array (CH_2) and also on the Kendrick mass defect difference among the y array (H_2). Then, the calculation was achieved for all peaks and molecules which have the same heteroatom content (O_2Si, O_3Si or O_4Si) were assigned to the same class. Inside this class, different homologous series can be present among their Kendrick mass defect. The full description of the algorithm is given below.

Glossary

stepCH$_2$: the step in the x array (CH_2)

stepH$_2$: the step in the y array (H_2)

_: the accuracy on the steps

Li: size of the family

M_f: the different masses detected in the family

M_i: the different masses for the stage i

M: the different detected masses but not associated to a family

M_o: the originated mass for the calculation of the family

Description of the algorithm

Algorithm 1 getFamily(mp)

```
INITIALISATION
$M_f = [M_o]$
$M_i = [M_o]$
$M_{i+1}$ = empty
$M\_ = [M_o]$
while Li not empty do
    for j = 1→size($L_i$) do
        km = $M_i^j$.km
        kmd = $M_i^j$.kmd
        v = [(km + $s_{H2}$ , kmd), (km, kmd + $s_{CH2}$ ), (km - $s_{H2}$ , kmd), (km, kmd - $s_{CH2}$ )]
        for k = 1 → size(v) do
            if $\exists m \in M$ abs(m.km – $v_k$.km) < $\varepsilon$ AND abs(m.kmd – $v_k$.kmd) < $\varepsilon$
            then
                M -= m
                $M_{i+1}$ += m;
            end if
        end for
    end for
    $M_f$ += $M_i$
    $M_i = [M_{i+1}]$
    $M_{i+1}$ = empty
end while
```

2-Isotope profile of ^{29}Si and ^{13}C for a better assignment of raw formula

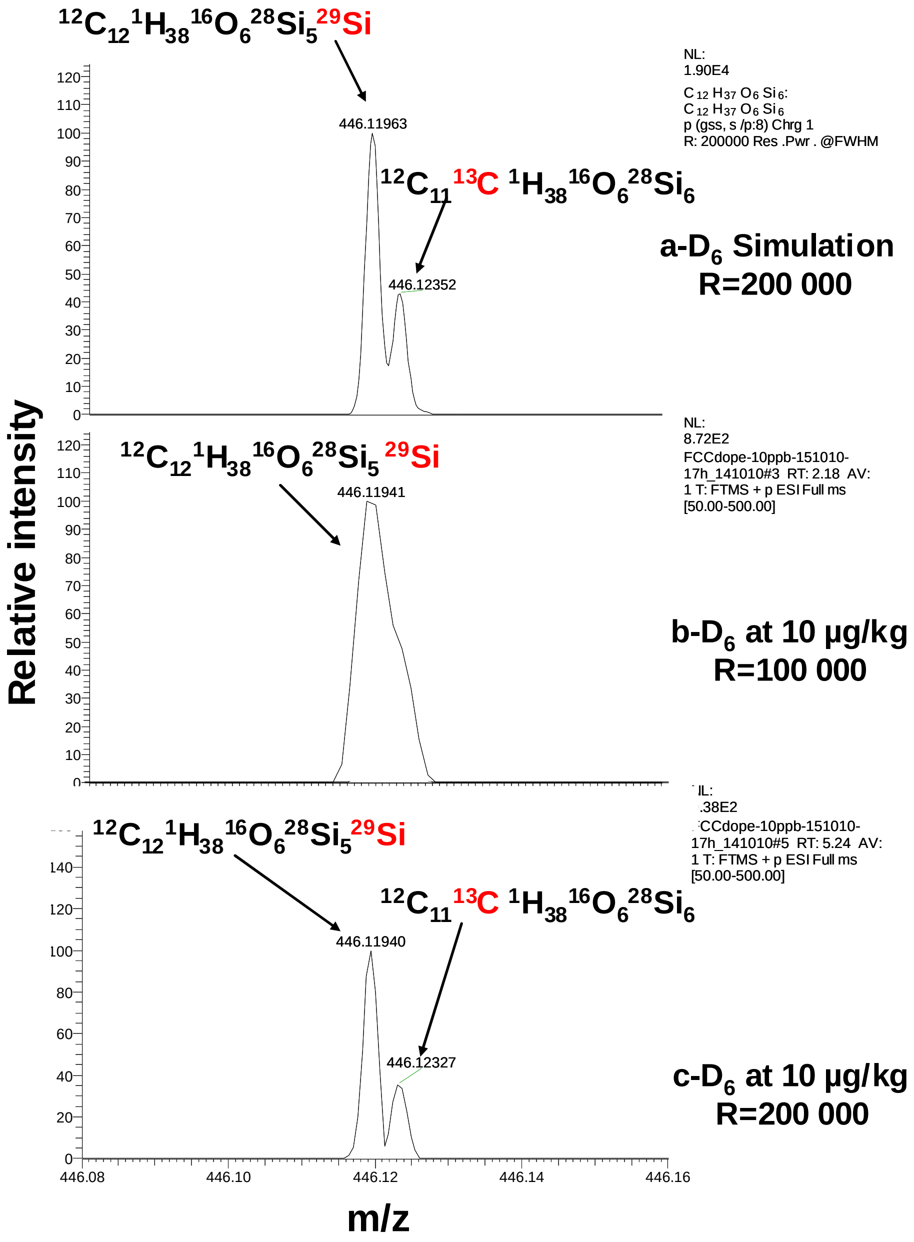


Figure A 1. Zoom of high resolution mass spectrum simulation (a) and real mass spectrum obtained for D_6 injected at 10 µg.kg^{-1} in spiked gasoline with an ESI-FT-ICR/MS acquisition (64 µscans and resolution of 100,000 (b) 200,000 (c) at m/z 400)

Figure c illustrates the separation of ^{29}Si and ^{13}C isotopes compared to isotopic simulation for D_6 molecule (a) with a resolution of 200,000. The relative abundance measured of ^{13}C isotope is around 40% of ^{29}Si isotope (c) which is in total agreement with the simulation (a). The raw formula and measured masses are indicated in each mass spectrum. Mass error of 0.52 and 0.25 ppm are measured for $^{12}C_{12}{}^{1}H_{38}{}^{16}O_6{}^{28}Si_5{}^{29}Si$ and $^{12}C_{11}{}^{13}C{}^{1}H_{38}{}^{16}O_6{}^{28}Si_6$ respectively.

3-Mass spectrum and Kendrick Plot of gasoline 5

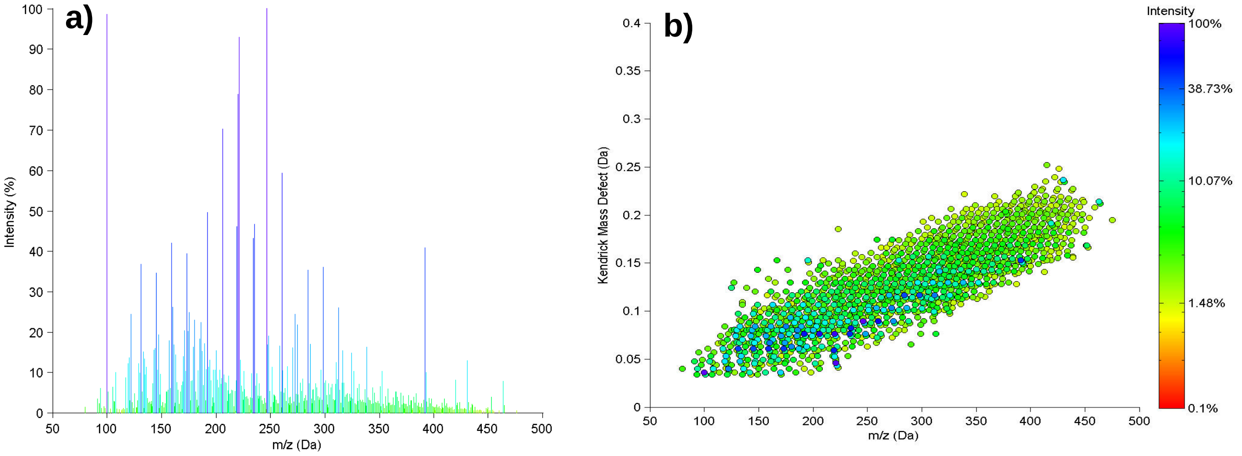


Figure A 2. Mass spectrum (a) and Kendrick plot (b) of gasoline 5 sample after the steam cracking process. The mass spectrum and Kendrick plot are obtained by the software taking into account all peaks with a S/N ratio >6σ of the baseline noise. The relative intensity is represented by a colour scale, from red to blue. The Kendrick plot showed the characterization of compounds horizontally according to number of CH_2 groups (homologous series) and vertically according to class (heteroatom composition) and type (double bond equivalent) between m/z 50 and 500

4-Elemental compositions of silicon compounds

Table A 1. Elemental composition assignments for (a) Dn, (b) O2Si, (c) O3Si and (d) O4Si classes characterized in naphtha 2 and in all investigated samples

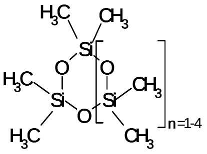
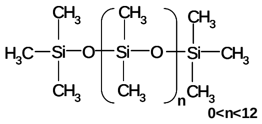
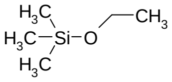
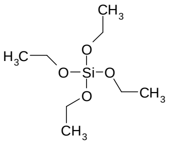
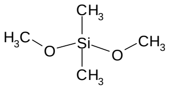
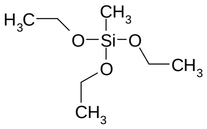
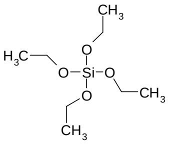
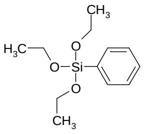
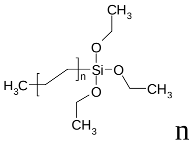
Measured mass	Relative intensity (%)	Theoretical mass	Mass error (ppm)	KMD	DBE	$[M+H]^+$ Formula	Samples ^{a}
a) Cyclic siloxanes (D_n)							
223.06369	0.660	223.06365	0.04	0.185	1	$C_6H_{19}O_3Si_3$	N1-2-G3-5
297.08250	0.064	297.08244	0.06	0.249	1	$C_8H_{25}O_4Si_4$	N1-2-G3-5
371.10100	0.732	371.10123	-0.18	0.313	1	$C_{10}H_{31}O_5Si_5$	N1-2-G3-5
445.11985	2.149	445.12002	-0.17	0.377	1	$C_{12}H_{36}O_6Si_6$	N1-2-G3-5
b) O_2Si Class							
105.03684	0.063	105.03663	0.21	0.080	1	$C_3H_9O_2Si$	N1-N2
119.05248	0.996	119.05228	0.20	0.080	1	$C_4H_{11}O_2Si$	N1-N2
131.05247	0.095	131.05228	0.19	0.094	2	$C_5H_{11}O_2Si$	N1
133.06814	7.897	133.06793	0.67	0.080	1	$C_5H_{13}O_2Si$	N2-G5
143.05246	0.454	143.05228	0.18	0.107	3	$C_6H_{11}O_2Si$	G5
145.06807	0.231	145.06793	0.21	0.094	2	$C_6H_{13}O_2Si$	N1-G5
147.08394	0.275	147.08358	0.20	0.080	1	$C_6H_{15}O_2Si$	N1-G5
157.06812	0.198	157.06793	0.19	0.107	3	$C_7H_{13}O_2Si$	N2-G5
159.08377	0.121	159.08358	0.18	0.094	2	$C_7H_{15}O_2Si$	N1-N2
161.09943	2.973	161.09923	0.19	0.080	1	$C_7H_{17}O_2Si$	N1-N2
169.06826	0.081	169.06793	0.33	0.120	4	$C_8H_{13}O_2Si$	N2
171.08378	0.275	171.08358	0.20	0.107	3	$C_8H_{15}O_2Si$	N2
173.09943	0.166	173.09923	0.19	0.094	2	$C_8H_{17}O_2Si$	N1-N2
175.11508	1.185	175.11488	0.19	0.080	1	$C_8H_{19}O_2Si$	N1-N2
185.09944	0.317	185.09923	0.21	0.107	3	$C_9H_{17}O_2Si$	N2
187.11505	0.160	187.11488	0.17	0.094	2	$C_9H_{19}O_2Si$	N1-N2
189.13073	0.514	189.13053	0.20	0.080	1	$C_9H_{21}O_2Si$	N1-N2
199.11508	0.360	199.11488	0.20	0.107	3	$C_{10}H_{19}O_2Si$	N2
201.13075	0.180	201.13053	0.22	0.094	2	$C_{10}H_{21}O_2Si$	N1-N2
203.14633	0.154	203.14618	0.14	0.080	1	$C_{10}H_{23}O_2Si$	N1-N2
211.11507	0.169	211.11488	0.19	0.120	3	$C_{11}H_{19}O_2Si$	N2
213.13070	0.362	213.13053	0.17	0.107	3	$C_{11}H_{21}O_2Si$	N2
215.14636	0.123	215.14618	0.18	0.094	2	$C_{11}H_{23}O_2Si$	N2
227.14638	0.212	227.14618	0.20	0.107	3	$C_{12}H_{23}O_2Si$	N2
241.16200	0.153	241.16183	0.17	0.107	3	$C_{13}H_{25}O_2Si$	N2
255.17753	0.084	255.17748	0.05	0.107	3	$C_{14}H_{27}O_2Si$	N2
269.19314	0.078	269.19313	0.01	0.107	3	$C_{15}H_{29}O_2Si$	N2
283.20892	0.067	283.20878	0.14	0.107	3	$C_{16}H_{31}O_2Si$	N2
291.17736	0.094	291.17748	-0.12	0.148	6	$C_{17}H_{27}O_2Si$	N2
293.19322	0.124	293.19313	0.08	0.134	5	$C_{17}H_{29}O_2Si$	N2
295.20883	0.175	295.20878	0.04	0.120	4	$C_{17}H_{31}O_2Si$	N2
297.22461	0.713	297.22443	-0.97	0.107	3	$C_{17}H_{33}O_2Si$	N2
309.22494	0.053	309.22443	0.50	0.120	4	$C_{18}H_{33}O_2Si$	N2

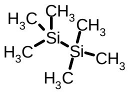
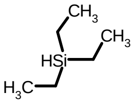
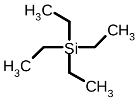
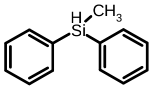
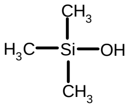
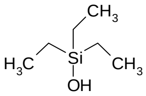
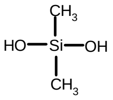
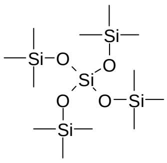
Measured mass	Relative intensity (%)	Theoretical mass	Mass error (ppm)	KMD	DBE	$[M+H]^+$ Formula	Samples [a]
c) O_3Si Class							
109.03177	0.205	109.03155	0.22	0.090	0	$C_2H_9O_3Si$	N1
123.04738	0.277	123.04720	0.21	0.090	0	$C_3H_{11}O_3Si$	N1
135.04741	0.135	135.04720	0.18	0.103	1	$C_4H_{11}O_3Si$	N1-N2
137.06304	0.092	137.06285	0.20	0.090	0	$C_4H_{13}O_3Si$	N1
149.06303	0.610	149.06285	0.20	0.103	1	$C_5H_{13}O_3Si$	N1-N2
151.07867	0.051	151.07850	0.17	0.090	0	$C_5H_{15}O_3Si$	N1
161.06267	0.158	161.06285	-0.71	0.117	2	$C_6H_{13}O_3Si$	N1-N2
175.07869	0.141	175.07850	-1.06	0.117	2	$C_7H_{15}O_3Si$	G5
163.07869	1.144	163.07850	0.20	0.103	1	$C_6H_{15}O_3Si$	G5
165.09436	0.120	165.09415	0.15	0.090		$C_6H_{17}O_3Si$	N1-N2-G5
177.09432	0.445	177.09456	-0.20	0.103	1	$C_7H_{17}O_3Si$	N1-N2
179.10999	0.148	179.10980	0.19	0.090	0	$C_7H_{19}O_3Si$(H)	N1-N2
191.10994	0.152	191.10980	0.19	0.103	1	$C_8H_{19}O_3Si$	N1-N2
193.12566	0.131	193.12545	0.18	0.090	0	$C_8H_{21}O_3Si$	N1-N2
205.12562	0.124	205.12545	0.17	0.103	1	$C_9H_{21}O_3Si$	N1
d) O_4Si Class							
181.08925	0.188	181.08906	-0.11	0.113	0	$C_6H_{17}O_4Si$	N1-N2
195.10489	0.811	195.10471	-0.55	0.113	0	$C_7H_{19}O_4Si$	N2-N1-G3
209.12056	0.886	209.12036	0.18	0.113	0	$C_8H_{21}O_4Si$ (D)	N1-2-G3-5
223.13615	0.291	223.13601	0.15	0.113	0	$C_9H_{23}O_4Si$	N1-N2
237.15184	0.095	237.15166	0.18	0.113	0	$C_{10}H_{25}O_4Si$	N1

[a] Measured mass, intensity, mass error are indicated for silicon compounds characterized in naphtha 2 when the molecule is characterized in several samples and in the indicated sample for others cases.

The relative intensity (%) was calculated from the compound with the maximum peak intensity for each sample.

Annexe 5 : Model silicon compound properties

Molecules (Abbreviations)	Raw formula	BP (°C)	MM (g.mol^{-1})	Chemical Structure
Cyclic siloxanes				
Hexamethylcyclotrisiloxane (D_3)	$C_6H_{18}O_3Si_3$	134	222	
Octamethylcyclotetrasiloxane (D_4)	$C_8H_{24}O_4Si_4$	175	296	
Decamethylcyclopentasiloxane (D_5)	$C_{10}H_{30}O_5Si_5$	211	370	
Dodecamethylcyclohexasiloxane (D_6)	$C_{12}H_{36}O_6Si_6$	245	444	
Linear siloxanes				
Hexamethyldisiloxane (L_2)	$C_6H_{18}OSi_2$	100	162	
Octamethyltrisiloxane (L_3)	$C_8H_{24}O_2Si_3$	153	236	
Decamethyltetrasiloxane (L_4)	$C_{10}H_{30}O_3Si_4$	194	310	
Dodecamethylpentasiloxane (L_5)	$C_{12}H_{36}O_4Si_5$	210	384	
Linear PDMS (L_6-L_{14})	--	--	458-974	
Ethoxysilanes				
Ethoxytrimethylsilane (I)	$C_5H_{14}OSi$	118	75	
Triethoxymethylsilane (H)	$C_7H_{18}O_3Si$	178	141	
Dimethoxydimethylsilane (DMDS)	$C_4H_{12}SiO_2$	120	81	
Triethoxymethylsilane (H)	$C_7H_{18}O_3Si$	143	178	
Tetraethoxysilane (D)	$C_8H_{20}O_4Si$	168	208	
Phenyltriethoxysilane (B)	$C_{12}H_{20}SiO_3$	265	240	
Triethoxyoctylsilane (C)	$C_{14}H_{32}O_3Si$	168	276	 n=6

Molecules (Abbreviations)	Raw formula	BP (°C)	MM (g.mol^{-1})	Chemical Structure
Silanes				
Hexamethyldisilane (E)	$C_6H_{18}Si_2$	146	112	
Triethylsilane (F)	$C_6H_{16}Si$	116	107	
Tetraethylsilane (K)	$C_8H_{20}Si$	144	153	
Diphenylmethylsilane (J)	$C_{13}H_{14}Si$	266	198	
Silanols and siloxandiols				
Trimethylsilanol (TMSOH)	$C_3H_{10}SiO$	90	98	
Triethylsilanol (TESOH)	$C_6H_{16}OSi$	132	158	
Dimethylsilanediol (DMSD)	$C_2H_8O_2Si$	100	92	
Internal standard				
Tetrakis(trimethylsilyloxy)silane (M_4Q)	$C_{12}H_{36}O_4Si_5$	106	384	

Annexe 6 : Supporting information de la section 7.2

Supporting information-Characterization of silicon molecules issued from PDMS degradation under thermal cracking of hydrocarbons: Part 2-Liquid samples analysis by a multi-technical approach based on gas chromatography and mass spectrometry

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A-Retention indices (I)

To recognize silicon compounds by a unique retention value in GC, the retention time of silicon compounds determined by GC/MS were converted into index of retention (I) to further allow the detection by GC-GC/TOFMS [287]. Figure A3 presents the scheme of a reference chromatogram containing a silicon compound (X) with two cyclic siloxanes compounds (D_n). Cyclic siloxanes (D_3-D_{17}) were present in all samples and their retention times using each hyphenated technique were determined. These compounds were chosen to be the reference compounds to calibrate the retention index. The retention time of each silicon compound was converted in retention index (I) thanks to the retention times of the two cyclic siloxanes eluted just before (t_RD_n) and after (t_RD_{n+1}) the target molecule (X) following the Eq 1. According to this unique retention index (I), the retention time of each silicon compound can be evaluated especially to determine the time of cuts using the GC-GC/TOFMS following the Eq 2.

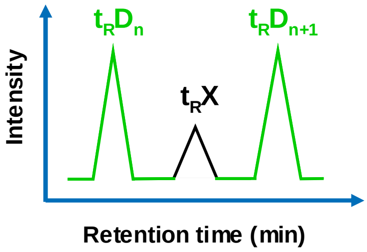


Figure A 3. Scheme of a chromatogram illustrating the retention times calibration used for the calculation of the index (I) of silicon compound (X). Cyclic siloxanes (D_n) were the peaks used as reference for the calculation

$$I = \left(\frac{(t_R X - t_R D_n)}{(t_R D_{n+1} - t_R D_n)}\right) + n \qquad (1)$$

Where t_R (min) is the retention time and n is the number of silicon atom in the reference molecule

$$t_R X = [(I - n)(t_R D_{n+1} - t_R D_n)] + t_R D_n \qquad (2)$$

B-Elemental compositions of silicon compounds characterized by ESI-FT-ICR/MS

Table A 2. List of silicon compounds characterized in PDMS degradation samples with their masses (measured and theoretical), mass error, formula $[M+H]^+$ of the molecule obtained using ESI-FT-ICR/MS

Measured Mass	Theoretical Mass	Mass Error (ppm)	Formula $[M+H]^+$
(1) Cyclic siloxanes			
223.06366	223.06365	0.01	$C_{6} H_{19} O_{3} Si_{3}$
297.08243	297.08244	-0.01	$C_{8} H_{25} O_{4} Si_{4}$
371.10118	371.10123	-0.05	$C_{10} H_{31} O_{5} Si_{5}$
445.11993	445.12002	-0.09	$C_{12} H_{37} O_{6} Si_{6}$
519.13896	519.13882	0.28	$C_{14} H_{43} O_{7} Si_{7}$
593.1581	593.15802	0.14	$C_{16} H_{49} O_{8} Si_{8}$
667.17705	667.1764	0.98	$C_{18} H_{55} O_{9} Si_{9}$
741.19607	741.19519	1.19	$C_{20} H_{61} O_{10} Si_{10}$
(3) α,ω-Dihydroxypolydimethylsiloxanes			
167.05545	167.05542	0.14	$C_{4} H_{15} O_{3} Si_{2}$
241.07423	241.07422	0.05	$C_{6} H_{21} O_{4} Si_{3}$
315.09306	315.09301	0.17	$C_{8} H_{27} O_{5} Si_{4}$
389.11177	389.1118	-0.07	$C_{10} H_{33} O_{6} Si_{5}$
463.13043	463.13059	-0.35	$C_{12} H_{39} O_{7} Si_{6}$
537.16482	537.16464	0.33	$C_{14} H_{45} O_{6} Si_{7}$
611.16887	611.16817	1.15	$C_{16} H_{51} O_{9} Si_{8}$
685.18778	685.18696	1.19	$C_{18} H_{57} O_{10} Si_{9}$
(4-a) Hydroxy methyl cyclic siloxanes			
225.04293	225.04292	0.01	$C_{5} H_{17} O_{4} Si_{3}$
299.06169	299.0617	-0.01	$C_{7} H_{23} O_{5} Si_{4}$
373.08045	373.08049	-0.05	$C_{9} H_{29} O_{6} Si_{5}$
447.09926	447.09924	0.02	$C_{11} H_{35} O_{7} Si_{6}$
521.11888	521.11849	0.76	$C_{13} H_{41} O_{8}Si_{7}$
595.13707	595.13687	0.34	$C_{15} H_{47} O_{9} Si_{8}$
669.15611	669.15566	0.67	$C_{17} H_{53} O_{10} Si_{9}$
(4-b) Methyl (hydroxyethyl) cyclic siloxanes			
253.07424	253.07422	0.02	$C_{7} H_{21} O_{4} Si_{3}$
327.09299	327.093	-0.01	$C_{9} H_{27} O_{5} Si_{4}$
401.11178	401.11179	-0.01	$C_{11} H_{33} O_{6} Si_{5}$
475.13055	475.13054	0.01	$C_{13} H_{39} O_{7} Si_{6}$
549.14995	549.14979	0.38	$C_{15} H_{45} O_{8} Si_{7}$
623.16893	623.16858	0.55	$C_{17} H_{51} O_{9} Si_{8}$
697.18811	697.18696	1.64	$C_{19} H_{57} O_{10} Si_{9}$
(5) Cyclic silanone or Bis(cyclosiloxanyl)siloxanes			
209.09597	209.09609	-0.12	$C_{4} H_{12} O_{4} Si_{3}$
283.03048	283.03041	0.08	$C_{6} H_{19} O_{5} Si_{4}$
357.04933	357.0492	0.13	$C_{8} H_{25} O_{6} Si_{5}$
431.06781	431.06799	-0.18	$C_{10} H_{31} O_{7} Si_{6}$
505.08729	505.08678	1.01	$C_{12} H_{36} O_{8} Si_{7}$
579.10627	579.10557	1.21	$C_{14} H_{42} O_{9} Si_{8}$
653.12536	653.12436	1	$C_{16} H_{49} O_{10} Si_{9}$
727.14417	727.14315	1.01	$C_{18} H_{55} O_{11} Si_{10}$

Measured Mass	Theoretical Mass	Mass Error (ppm)	Formula $[M+H]^+$
(6) α-hydroxy,ω-methyl polysiloxanes			
165.0757	165.07575	-0.05	$C_5 H_{16} O_2 Si_2$
239.09498	239.09495	0.03	$C_7 H_{23} O_3 Si_3$
313.11378	313.11374	0.04	$C_9 H_{29} O_4 Si_4$
387.13251	387.13253	-0.05	$C_{11} H_{35} O_5 Si_5$
461.15113	461.15132	-0.41	$C_{13} H_{41} O_6 Si_6$
535.17057	535.17012	0.46	$C_{15} H_{47} O_7 Si_7$
609.18713	609.18891	2.92	$C_{17} H_{53} O_8 Si_8$
(7-a) Methyl (methylhydroperoxy) cyclic siloxanes			
255.05355	255.05348	0.07	$C_6 H_{19} O_5 Si_3$
329.07234	329.07227	0.06	$C_8 H_{25} O_6 Si_4$
403.09099	403.09106	-0.17	$C_{10} H_{31} O_7 Si_5$
477.10939	477.10985	-0.96	$C_{12} H_{37} O_8 Si_6$
551.1287	551.12864	0.1	$C_{14} H_{43} O_9 Si_7$
(7-b) Methyl (propylhydroperoxy) cyclic siloxanes			
283.08455	283.08478	0.81	$C_8 H_{22} O_5 Si_3$
357.10351	357.10357	0.17	$C_{10} H_{29} O_6 Si_4$
431.12237	431.12236	-0.02	$C_{12} H_{35} O_7 Si_5$
(8) Sylene cyclic siloxanes			
207.03266	207.03276	-0.1	$C_5 H_{15} O_3 Si_3$
281.05116	281.05114	0.02	$C_7 H_{21} O_4 Si_4$
355.06989	355.06993	-0.04	$C_9 H_{27} O_5 Si_5$
429.08871	429.08872	-0.01	$C_{11} H_{33} O_6 Si_6$
503.10812	503.10792	0.39	$C_{13} H_{39} O_7 Si_7$
577.12698	577.12672	0.46	$C_{15} H_{45} O_8 Si_8$
651.14595	651.1451	1.3	$C_{17} H_{51} O_9 Si_9$
725.16505	725.16389	1.6	$C_{19} H_{57} O_{10} Si_{10}$
(9) Dimethoxy polysiloxanes			
121.06885	121.06793	0.92	$C_4 H_{13} O_2 Si$
195.08674	195.08672	0.01	$C_6 H_{19} O_3 Si_2$
269.1055	269.10552	-0.01	$C_8 H_{25} O_4 Si_3$
343.12434	343.12431	0.04	$C_{10} H_{31} O_5 Si_4$
417.14307	417.14309	-0.02	$C_{12} H_{37} O_6 Si_5$
491.16183	491.16184	0	$C_{14} H_{43} O_7 Si_6$
565.18153	565.18068	1.5	$C_{16} H_{49} O_8 Si_7$
639.19768	639.19674	0.94	$C_{18} H_{55} O_9 Si_8$
(10) Methylpropyl cyclic siloxanes			
251.095	251.09495	0.04	$C_8 H_{23} O_3 Si_3$
325.11372	325.11374	-0.02	$C_{10} H_{29} O_4 Si_4$
399.13268	399.132532	0.37	$C_{12} H_{35} O_5 Si_5$

The linear siloxanes (2: L_2-L_5), characterized using GC/MS SIM are not detected using ESI-FT-ICR/MS due their lower response factor and concentrations at trace levels [16].

Table A 3. List of higher molecular mass cyclic siloxanes characterized in PDMS degradation samples

D_n	Formula $[M+H]^+$
Higher molecular mass cyclic siloxanes	
D_{11}	$C_{22}\ H_{67}\ O_{11}\ Si_{11}$
D_{12}	$C_{24}\ H_{73}\ O_{12}\ Si_{12}$
D_{13}	$C_{26}\ H_{79}\ O_{13}\ Si_{13}$
D_{14}	$C_{28}\ H_{85}\ O_{14}\ Si_{14}$
D_{15}	$C_{30}\ H_{91}\ O_{15}\ Si_{15}$
D_{16}	$C_{32}\ H_{97}\ O_{16}\ Si_{16}$
D_{17}	$C_{34}\ H_{103}\ O_{17}\ Si_{17}$
D_{18}	$C_{36}\ H_{109}\ O_{18}\ Si_{18}$
D_{19}	$C_{38}\ H_{115}\ O_{19}\ Si_{19}$
D_{20}	$C_{40}\ H_{121}\ O_{20}\ Si_{20}$
D_{21}	$C_{42}\ H_{127}\ O_{21}\ Si_{21}$
D_{22}	$C_{44}\ H_{133}\ O_{22}\ Si_{22}$
D_{23}	$C_{46}\ H_{139}\ O_{23}\ Si_{23}$
D_{24}	$C_{48}\ H_{145}\ O_{24}\ Si_{24}$
D_{25}	$C_{50}\ H_{151}\ O_{26}\ Si_{25}$
D_{26}	$C_{52}\ H_{157}\ O_{26}\ Si_{26}$

Explanation

Based on the previous cyclic siloxanes characterized by their raw formula using the exact mass measurement of the ESI-FT-ICR/MS (<2 ppm) (Table A2), cyclic siloxanes with a degree of polymerization up to 26 were evidenced thanks to the repetition pattern C_2H_6OSi (m/z 74) (Table A3).

C-Example of EI, CI and MS^2 mass spectra for heptamethylhydroxy cyclotetrasiloxane

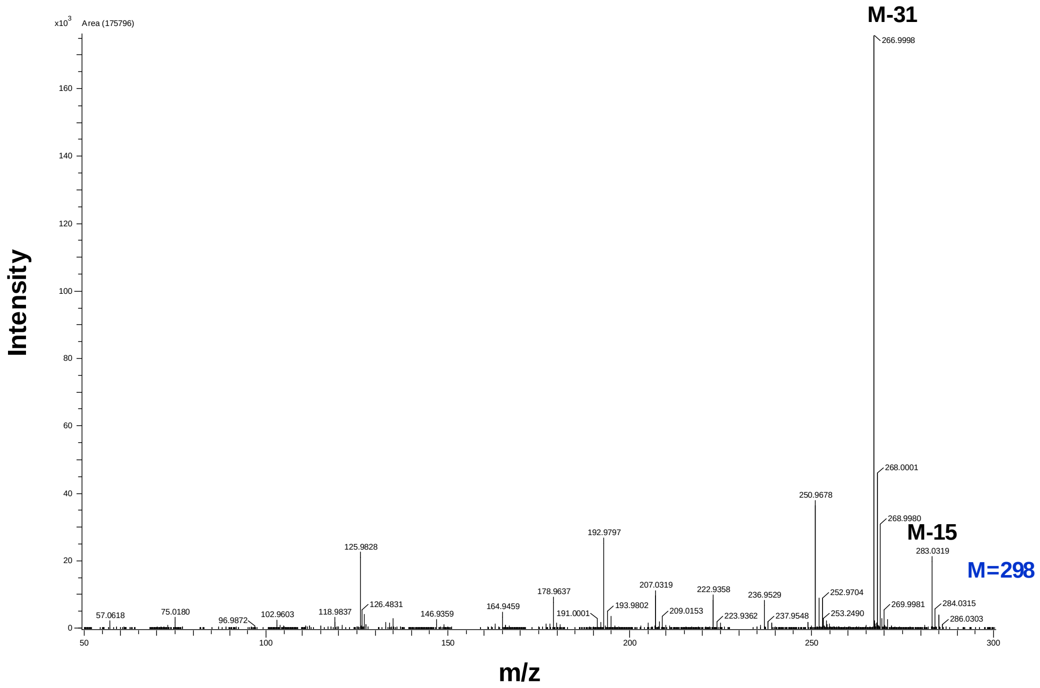


Figure A 4. EI mass spectrum of heptamethylhydroxy cyclotetrasiloxane (4-a) obtained for the test B by GC/TOFMS

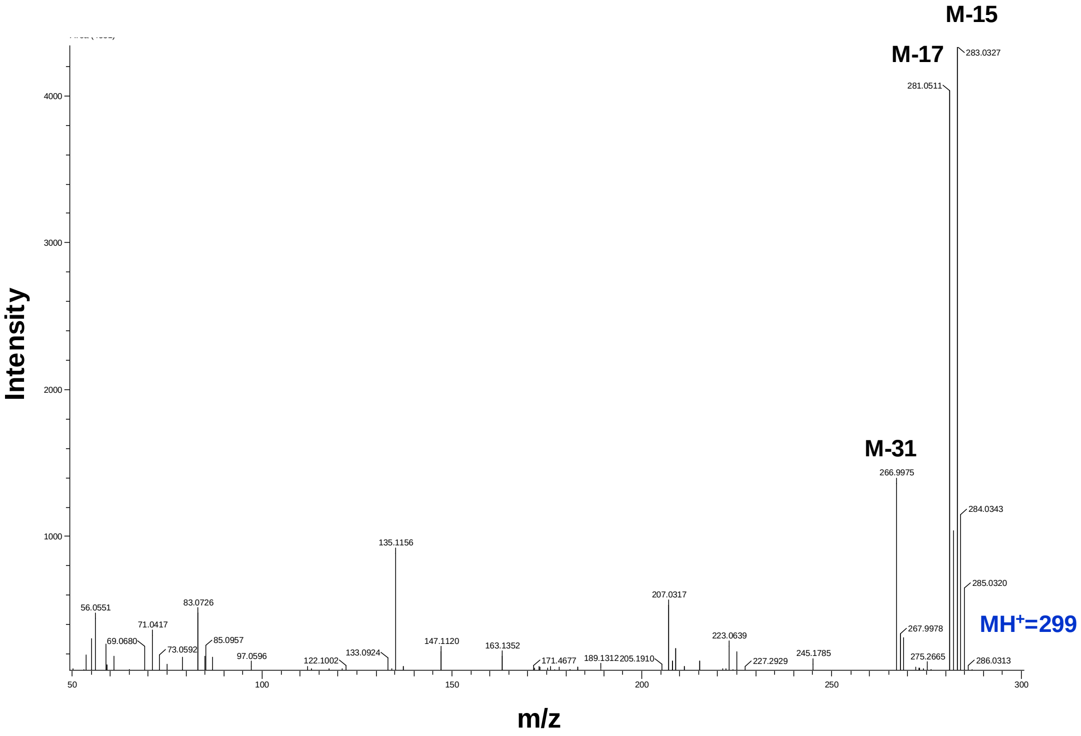


Figure A 5. CI mass spectrum of heptamethylhydroxy cyclotetrasiloxane (4-a) obtained for the test B by GC/TOFMS

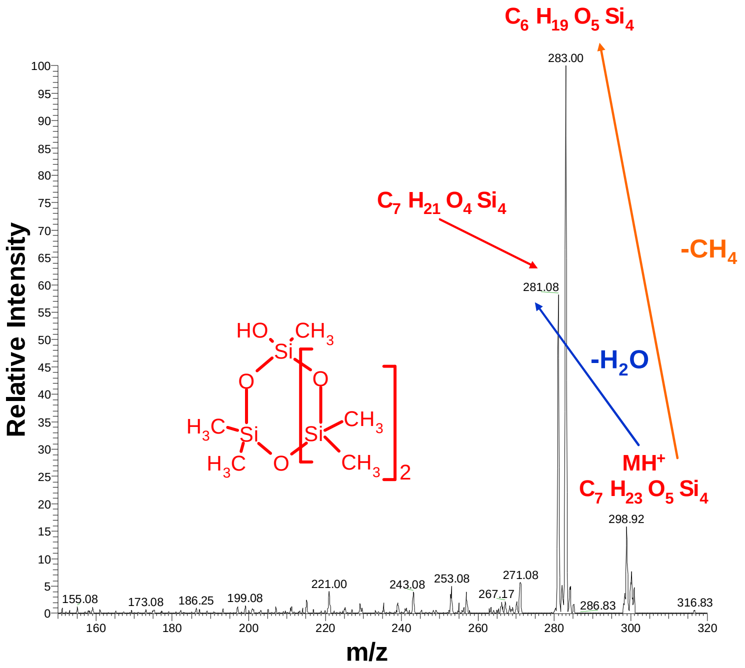


Figure A 6. MS^{2}spectrum obtained for the C_7 H_{22} O_5 Si_4 silicon compound using ESI/MS

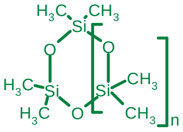
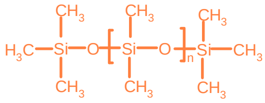
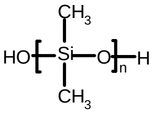
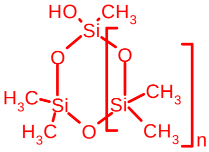
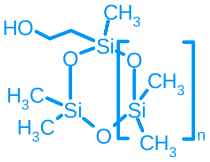
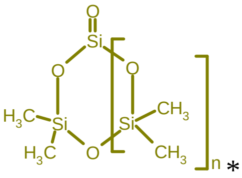
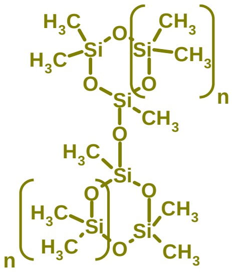
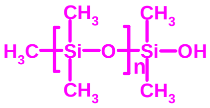
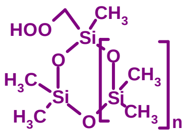
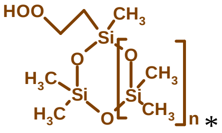
Explanation and extrapolation to other silicon compounds of the family

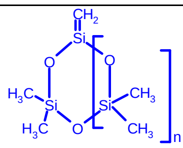
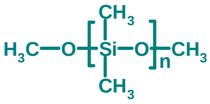
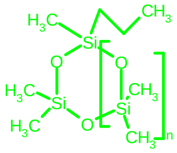
Heptamethylhydroxyl cyclotetrasiloxane was not commercially available. The chemical structure of this compound was validated thanks to the EI, CI and MS^2 mass spectra. The known cyclic siloxane D_4 loses a CH_4 group (M-15) from the protonated molecule in CI (Table A2). Similarly to these fragment ions, the heptamethylhydroxyl cyclotetrasiloxane loses methane. However, the CI mass spectrum (Figure A5) showed a peak at m/z 281, which matches to a loss of 18 from the MH$^+$. Similarly to siloxanediols, this was assigned to water elimination. This hypothesis was confirmed by the MS^2 spectrum (Figure A6) that demonstrated the loss of water from the protonated molecule (in blue) and the loss of CH_4 (in orange). The characterization of the others compounds of the family was achieved thanks to the repetition pattern C_2H_6OSi using the exact mass in FT-ICR/MS or using the retention times by GC-TOF/MS.

The Table A2 lists the different silicon compounds with their DBE, fragment ions in EI and CI obtained during the analysis of PDMS degradation samples using GC/TOFMS. These molecules were also characterized using FT-ICR/MS with an excellent mass accuracy (Table A4) and by MS^n to strengthen their chemical structure.

D-List of silicon compounds characterized in pdms degradation samples using mass spectrometry techniques

Table A 4. List of the silicon compounds characterized in PDMS degradation samples with their double bon equivalent (DBE), their fragment ions in chemical ionization (CI) and in electron ionization (EI), their fragments using MS^n and their chemical structure

N°	Molecules	DBE	Ions (CI)	Ions (EI)	MS^n	Chemical structure
(1)	Cyclic siloxanes	1	$MC_2H_5^+$ MH^+ M-15	M-15 M-31	Loss of CH$_4$	
(2)	Linear polydimethylsiloxanes	0	n.a.	M-15 M-31	n.a.	
(3)	α,ω-Dihydroxy polydimethylsiloxanes	0	M-17 M-33	M-33	n.a.	
(4)-a	Hydroxy methyl cyclic siloxanes	1	M-15 M-17 M-31	M-15 M-31	-Loss of CH$_4$ -Loss of H$_2$O	
(4)-b	Methyl (hydroxyethyl) cyclic siloxanes	1	M-15 M-31 M-45	M-31 M-45	-Loss of CH$_4$ -Loss of C$_2$H$_6$O	
(5)-a	Cyclic silanone	2	$MC_2H_5^+$ MH^+ M-15	M-15 M-31	Loss of CH$_4$	
(5)-b	Bis(cyclosiloxanyl)siloxanes	2	MH^+ M-15	M-15	-Loss of D$_n$ -Loss of D$_n$-OH -Loss of C$_4$H$_{12}$Si	
(6)	α-Hydroxy,ω-methyl polysiloxanes	0	M-15 M-17 M-31	M-15 M-31	-Loss of H$_2$O -Loss of C$_2$H$_6$O	
(7-a)	Methyl (methylhydroperoxy) cyclo siloxanes	1	M-31 M-47	M-47	-Loss of H$_2$O -Loss of C$_2$H$_4$O	
(7-b)	Methyl (propylhydroperoxy) cyclo siloxanes	1	MH^+ M-15	M-15 M-31	n.a.	

N°	Molecules	DBE	Ions (CI)	Ions (EI)	MS^n	Chemical structure
(8)	Sylene cyclic siloxanes	2	MH$^+$ M-13	M-13 M-15	Loss of CH_4	 *
(9)	Dimethoxy polysiloxanes	0	n.a.	M-15 M-31	-Loss of CH_4 -Loss of C_2H_6O	 $H_3C-O-[Si(CH_3)_2-O]_n-CH_3$
(10)	Methylpropyl cyclic siloxanes	1	n.a.	M-31 M-43 M-57	-Loss of C_2H_4 -Loss of C_3H_8	

n.a. not analyzed using this technique
* not strengthen by MS^n
For MS^n, 2<n<4

Annexe 7 : Spectres de Masse EI, CI and MS^n des composés Si$_4$ caractérisés dans le test de dégradation B

(1) Cyclic siloxanes (D$_n$)

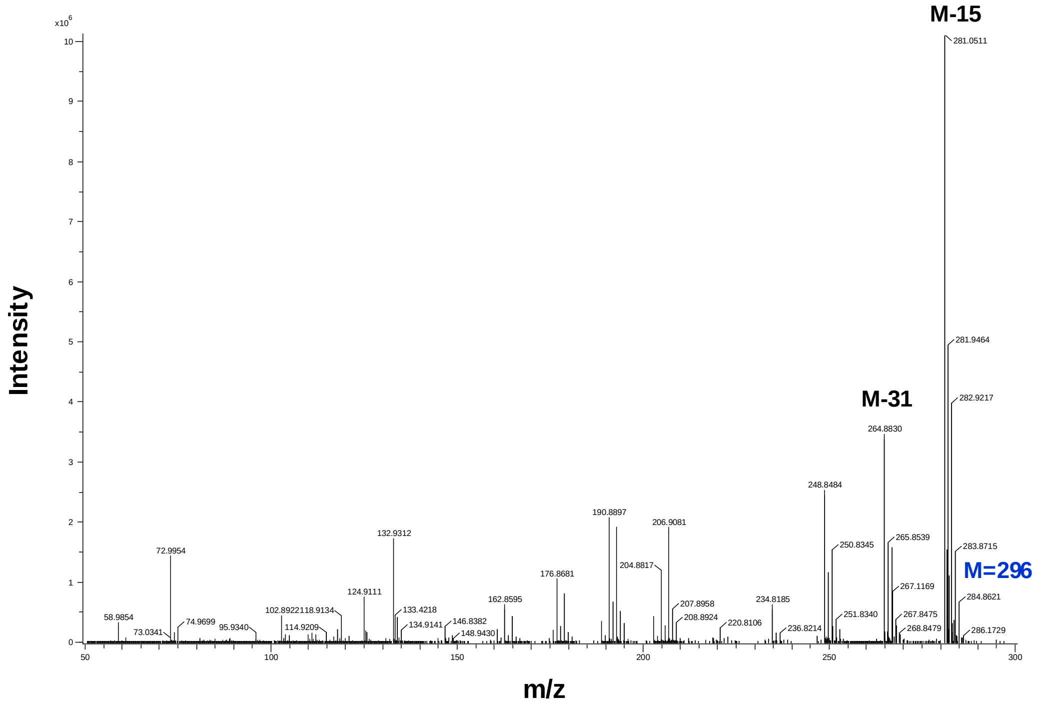


Figure A 7. S EI mass spectrum of octamethylcyclotetracyclosiloxane (D$_4$) obtained for the test B by GC/TOFMS

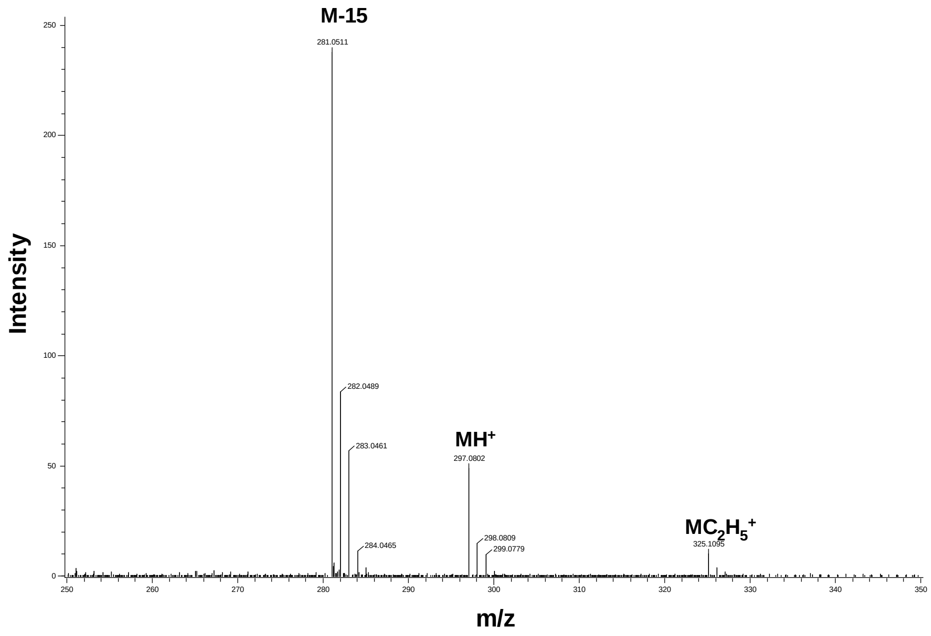
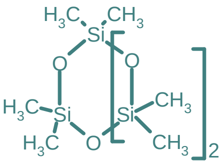


Figure A 8. S CI mass spectrum of octamethylcyclotetracyclosiloxane (D$_4$) obtained for the test B by GC/TOFMS

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_8 H_{24} O_4 Si_4$	1	296	325/297/281	281/365/249	

Validation

Octamethylcyclotetrasiloxane (D_4) was identified with the retention times of the commercially available standard and its mass spectra (Figure A7 (EI) and Figure A8 (CI)).

(2) Linear siloxanes (L_n)

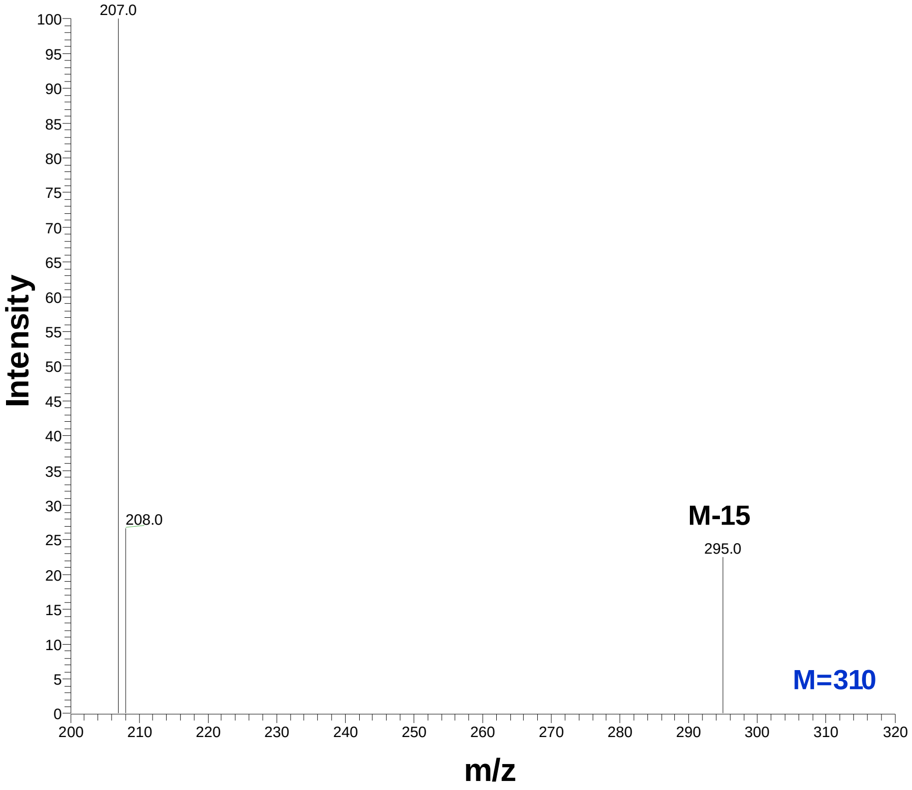
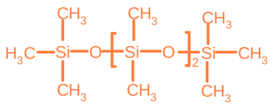


Figure A 9. EI mass spectrum for decamethyltetrasiloxane (L_4) obtained using GC/MS SIM

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_{10}H_{30}O_3Si_4$	0	310	Not detected	73/207/295	

Validation

Decamethyltetrasiloxane (L_4) was identified with the retention time of the commercially available standard and with its main ions using GC/MS SIM (Figure A9).

(3) Siloxanediols

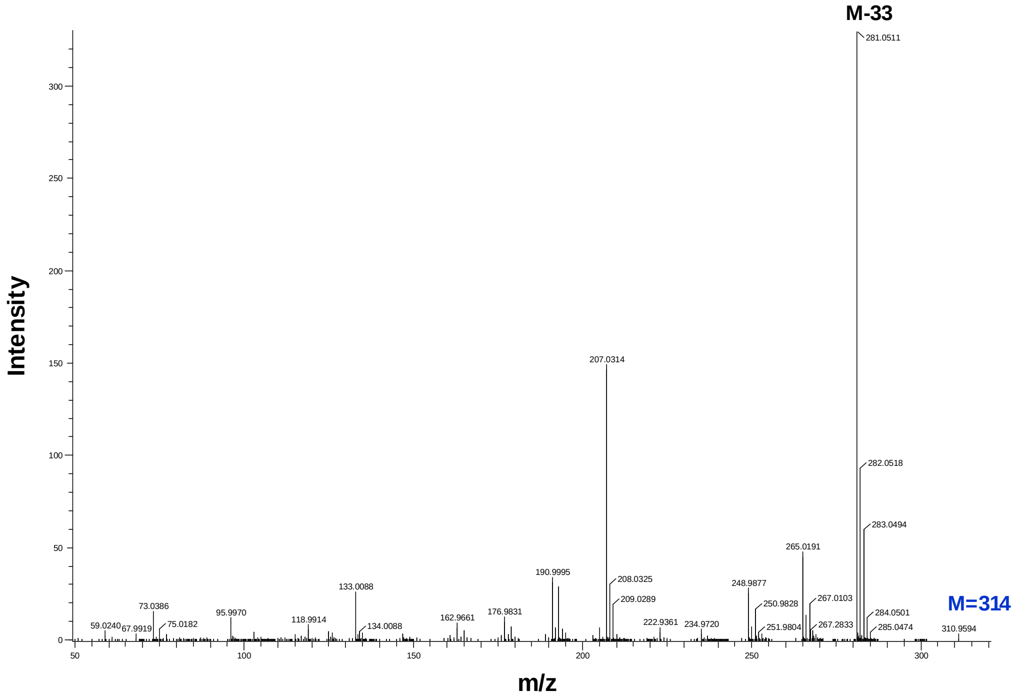


Figure A 10. EI mass spectrum of octamethyl-1,7-tetrasiloxanediol (OH-(Me$_2$SiO)$_4$-H)) obtained for the test B by GC/TOFMS

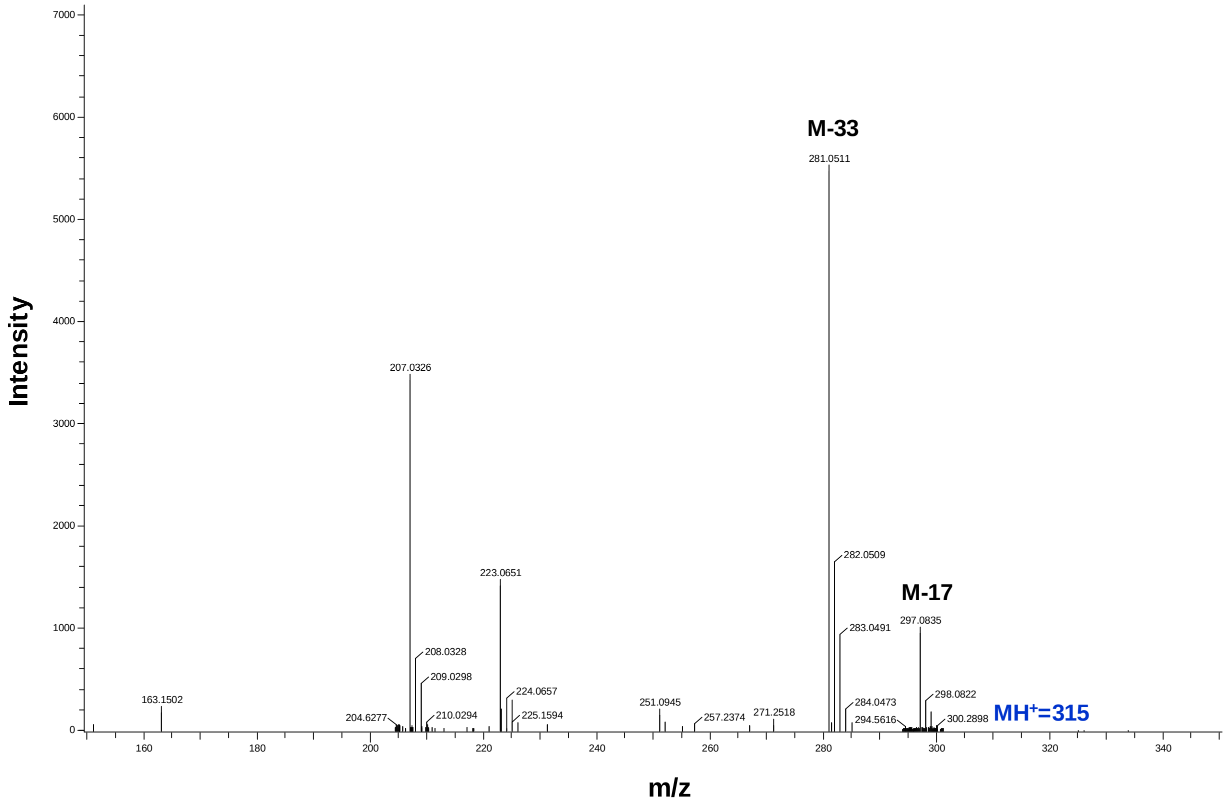
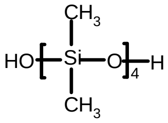


Figure A 11. CI mass spectrum of octamethyl-1,7-tetrasiloxanediol (OH-(Me$_2$SiO)$_4$-H)) obtained for the test B by GC/TOFMS

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_8H_{26}O_5Si_4$	0	314	297/281/207	281/265/249	 $HO{-}[Si(CH_3)_2{-}O]_4{-}H$

Validation

Octamethyl-1,7-tetrasiloxanediol ($HO\text{-}(Me_2SiO)_4\text{-}H$)) was identified thanks to its retention time ranging from the retention time of decamethylpentacyclosiloxane (D_5) and the retention time of Dodecamethylcyclohexasiloxane (D_6). This compound was also confirmed by its mass spectrum (Figure A10) as previously described in the paper and in Varaprath *et al.* [90]. Moreover, the presence of an M-17 peak in the CI mass spectrum (Figure A11) confirmed the loss of H_2O from the protonated molecule. This peak was systematically obtained in GC/TOFMS in CI mode when a Si-OH group is present in the structure. Each siloxanediol (Si_n) was eluted after each cyclic siloxane (Si_{n+1}). This trend was right for all compounds of this family with the same repetition pattern C_2H_6OSi. The characterization of the others compounds of the family was achieved thanks to the repetition pattern C_2H_6OSi using the exact mass in FT-ICR/MS or using the retention times by GC/TOFMS.

(4-a) Hydroxymethyl cyclic siloxanes

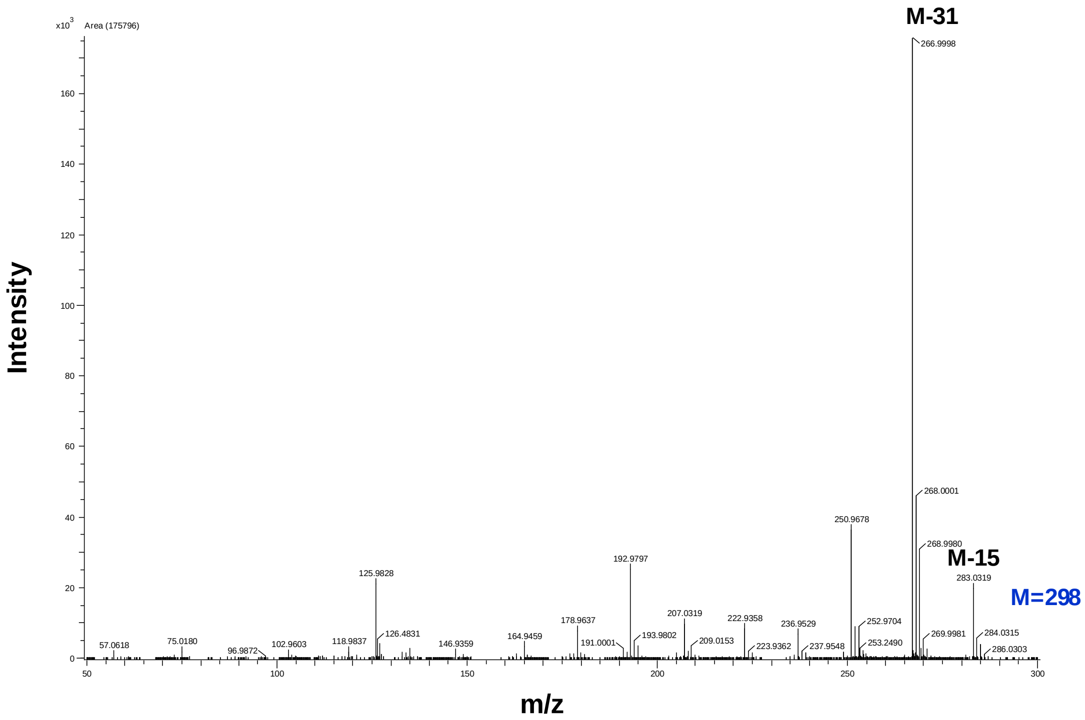


Figure A 12. EI mass spectrum of heptamethylhydroxy cyclotetrasiloxane obtained for the test B by GC/TOFMS

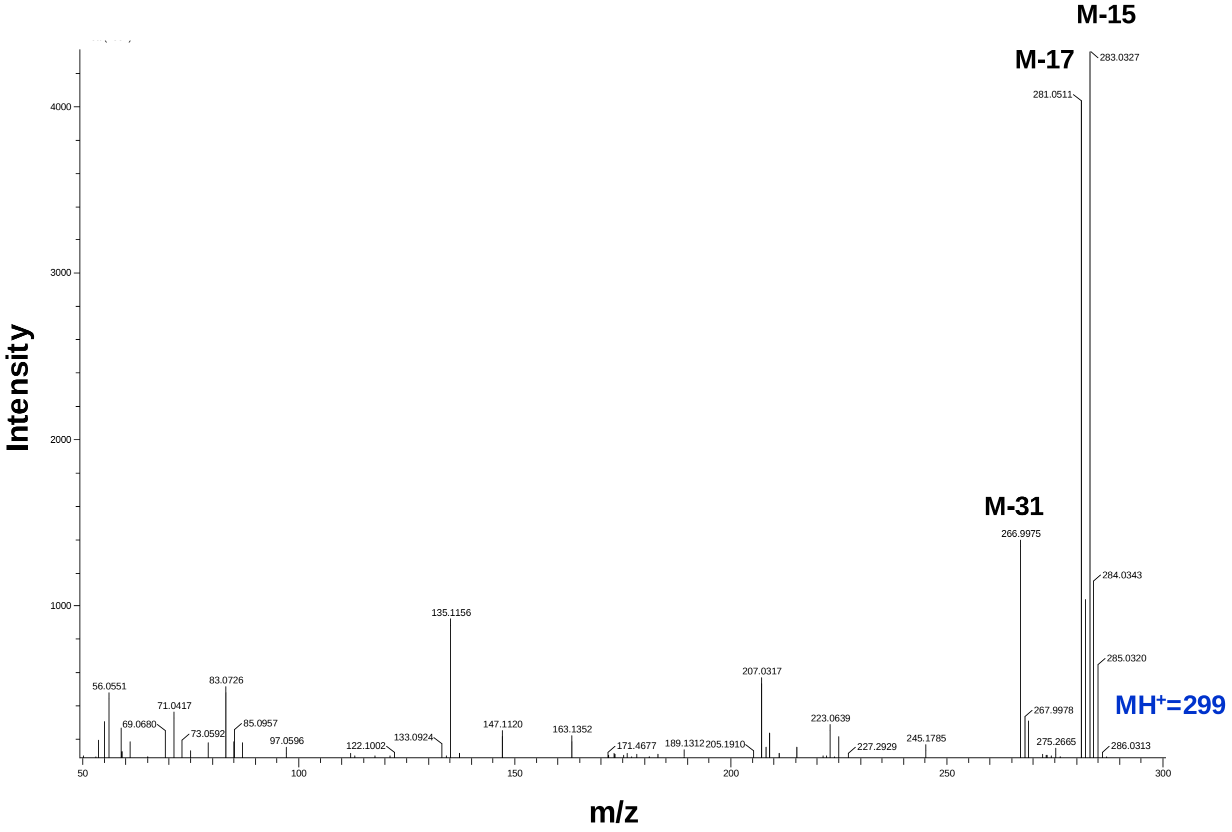


Figure A 13. CI mass spectrum of heptamethylhydroxy cyclotetrasiloxane obtained for the test B by GC/TOFMS

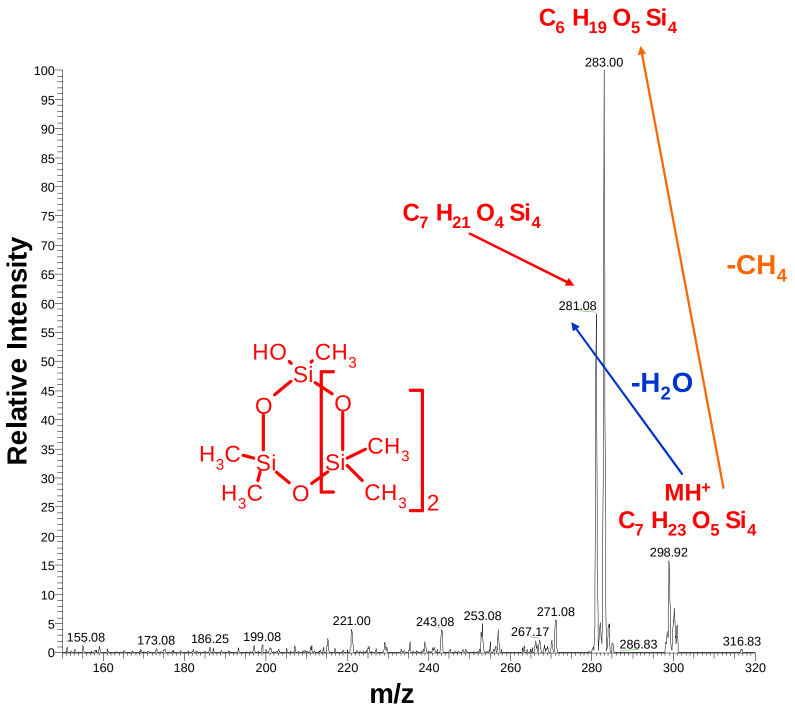
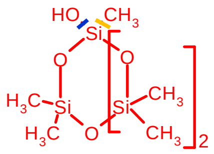


Figure A 14. MS^2 spectrum obtained for the $C_7 H_{22} O_5 Si_4$ silicon compound using ESI/MS

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_7 H_{22} O_5 Si_4$	1	298	283/281/267	283/267/251/126	

Validation

Heptamethylhydroxyl cyclotetrasiloxane was not commercially available. The chemical structure of this compound was validated thanks to the EI, CI and MS^2 mass spectrum. Similarly as the fragmentation of D_4, which loses a CH_3 group (M-15) in EI (Figure A12) fitted to the elimination of CH4 from the MH^+ in CI (Figure A13), this compound was constitued of a methyl group on the silicon atom. However, the CI mass spectrum (Figure A13) showed a peak at m/z 281, which matches to a loss of 18 from the MH^+. Similarly to siloxanediols, this was assigned to an OH group on the silicon atom. This hypothesis was strengthened by the MS^2 spectrum (Figure A14) that demonstrated the loss of water from the protonated molecule (in blue) and the loss of CH_4 (in orange). The characterization of the others compounds of the family was achieved thanks to the repetition pattern C_2H_6OSi using the exact mass in FT-ICR/MS or using the retention times by GC/TOFMS.

(4-b) Methyl (hydroxyethyl) cyclic siloxanes

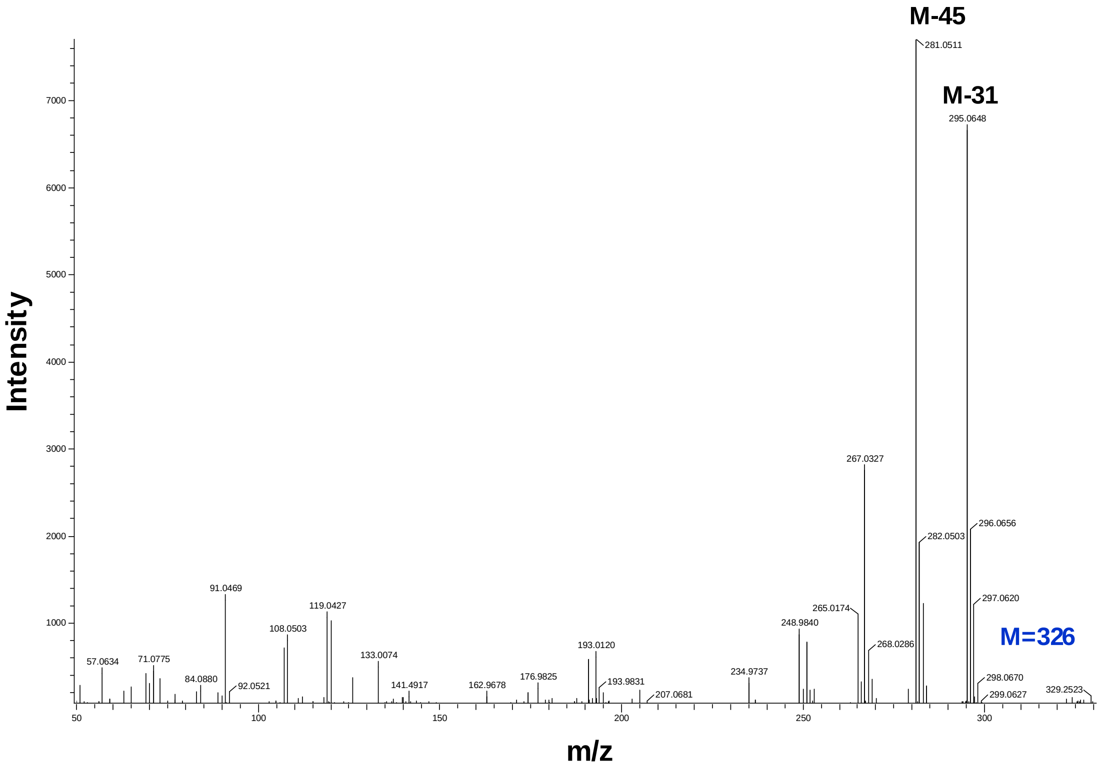


Figure A 15. EI mass spectrum of pentamethyl ethyl hydroxycyclotetrasiloxane ($C_9H_{26}O_5Si_4$) obtained for the test B by GC/TOFMS

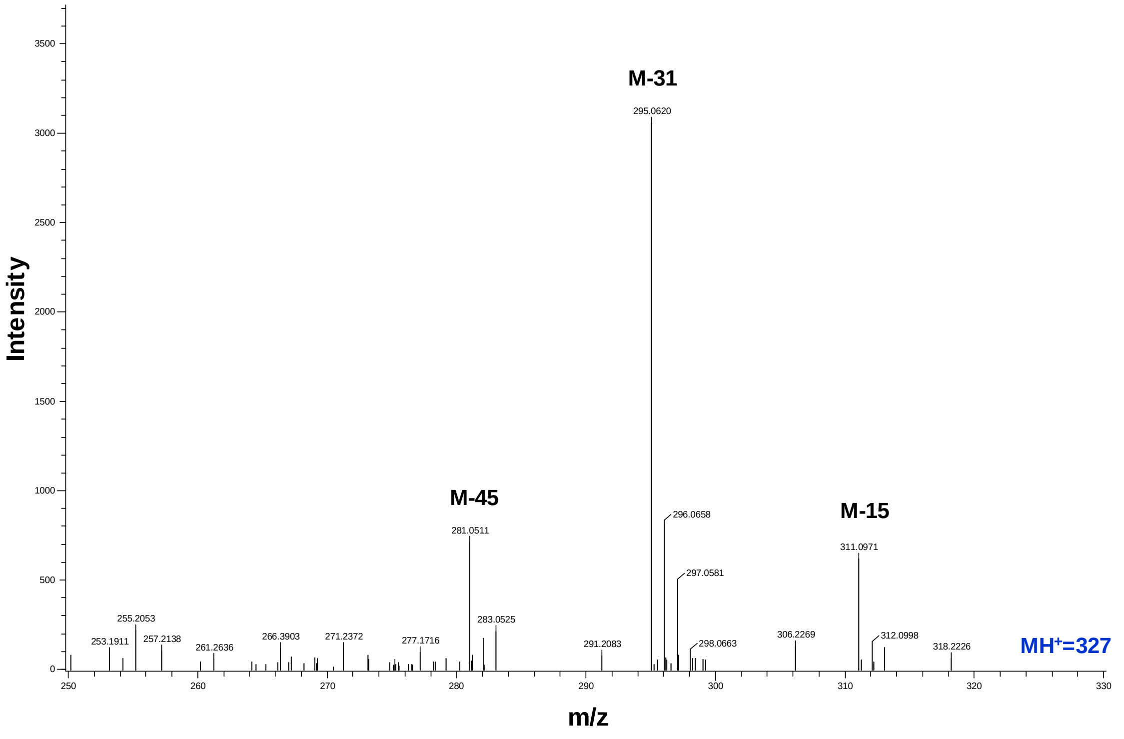


Figure A 16. CI mass spectrum of pentamethyl ethyl hydroxycyclotetrasiloxane ($C_9H_{26}O_5Si_4$) obtained for the test B by GC/TOFMS

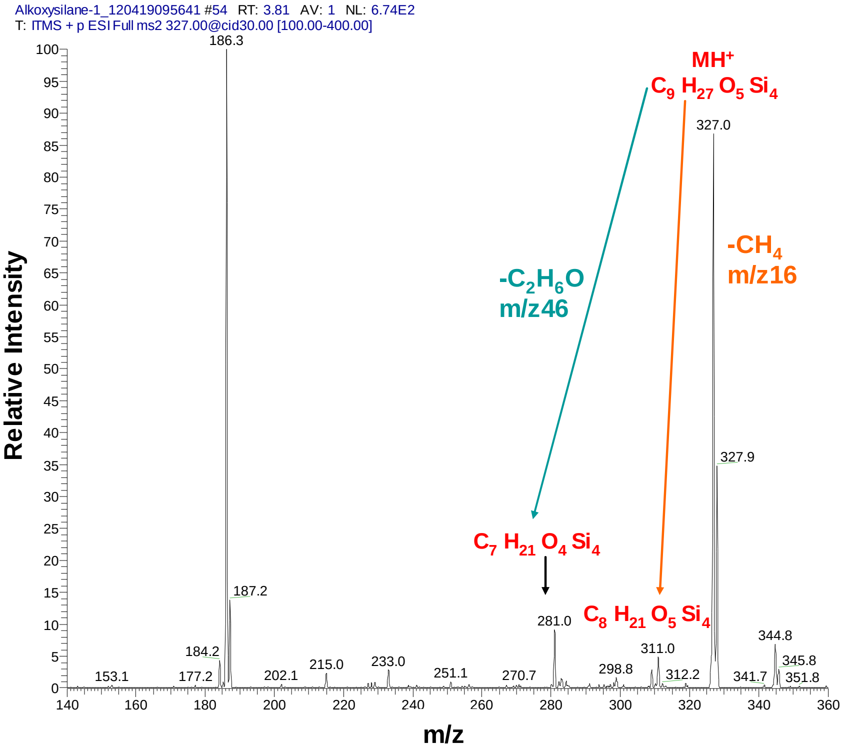
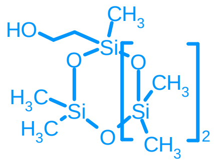


Figure A 17. MS^2 mass spectrum of pentamethyl ethyl hydroxycyclotetrasiloxane ($C_9H_{26}O_5Si_4$) using ESI/MS

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_9H_{26}O_5Si_4$	1	326	311/295/281	295/281/265/249/193	

Validation

The FT-ICR/MS analysis demonstrated that the $C_9H_{26}O_5Si_4$ molecule has also 1 unsaturation in its chemical structure similarly to the previous molecule identified as heptamethylhydroxy cyclotetrasiloxane ($C_7H_{22}O_5Si_4$) (4-a).

The CI mass spectrum showed the detection of three main ions respectively at m/z 311 (M-15), m/z 295 (M-31) and m/z 281 (M-45) from the protonated molecule $C_9H_{27}O_5Si_4$ (Figure A16). In the EI mass spectrum, the M-31 and M-45 peaks were confirmed (Figure A16). The M-31 is well-known and observed for D_4. This peak perfectly fitted with the scission of Si-CH_3 (m/z 15) bond followed by a second scission and a loss of CH_4 (m/z 16). The M-45 at m/z 281 peak matched with the loss of C_2H_5O (m/z 45) and demonstrated the presence of this group on the Si atom.

The MS^2 spectrum clearly strengthened the presence of these two groups on the cyclic siloxane structure with the detection of fragmented ions at m/z 311 and m/z 281 respectively fitted to the loss of CH_4 and C_2H_6O from the protonated molecule (m/z 327) (Figure A17). Thus, chemical structure was strengthened.

The characterization of the others compounds of the family was achieved thanks to the repetition pattern C_2H_6OSi using the exact mass in FT-ICR/MS or using the retention times by GC/TOFMS.

(5-a) Cyclic silanone

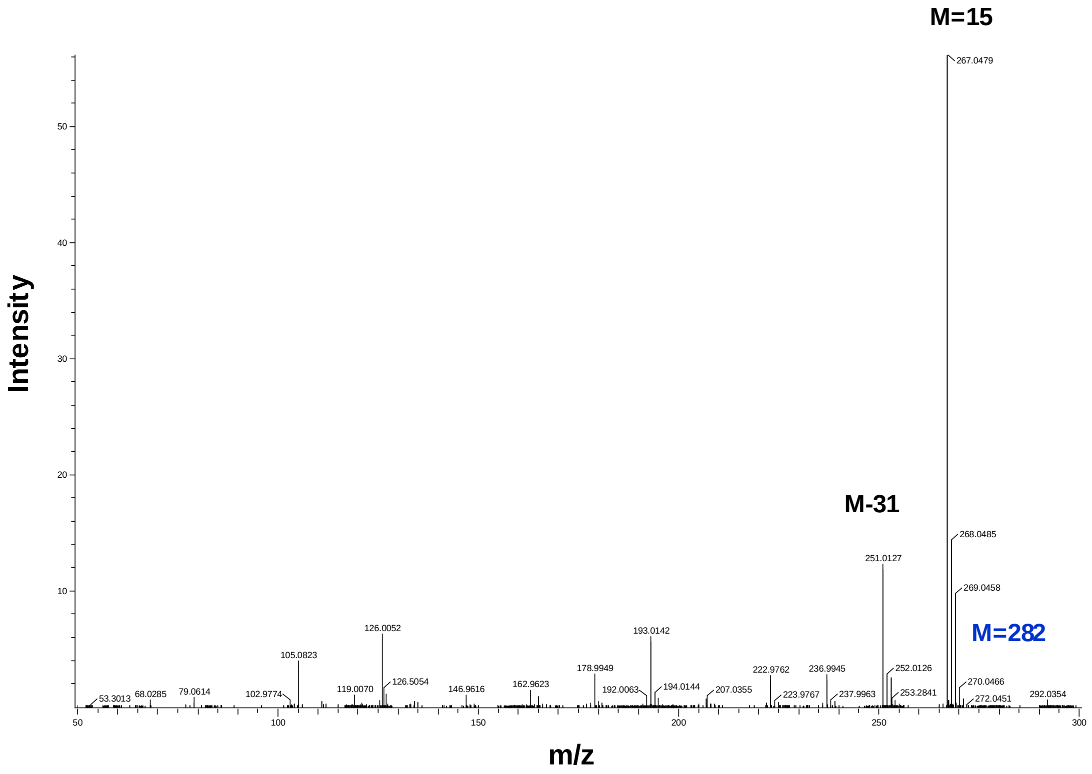


Figure A 18. EI mass spectrum of $C_6H_{19}O_5Si_4$ obtained for the test B by GC/TOFMS

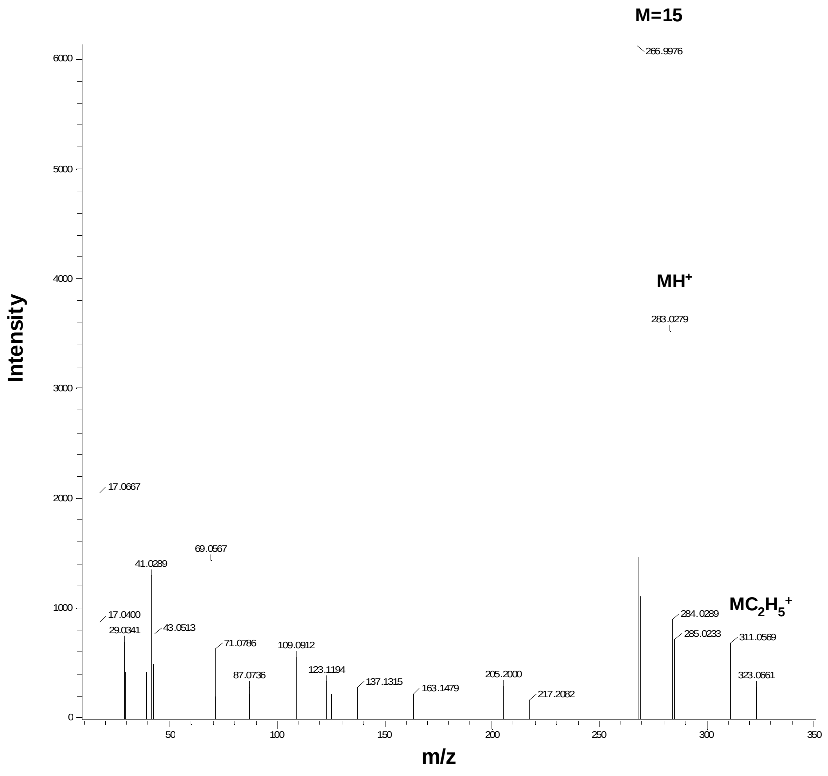
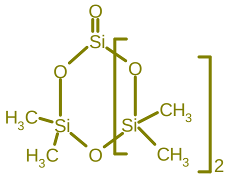


Figure A 19. CI mass spectrum of $C_6H_{19}O_5Si_4$ obtained for the test B by GC/TOFMS

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_6 H_{19} O_5 Si_4$	2	282	311/283/267	126/193/251/267	

Validation

The FT-ICR/MS analysis demonstrated that the $C_6 H_{19} O_5 Si_4$ molecule has two unsaturations in its chemical structure. Thanks to the GC/TOFMS in CI mode (Figure A19), this molecule was characterized by its retention time and also by its EI mass spectrum (Figure A18). Similarly to $C_7 H_{22} O_5 Si_4$ (D_4-OH), a M-15 peak at m/z 267 indicated the loss of CH_3. According to the DBE of 2 and to the same O_5Si_4 content than D_4-OH, the hexamethyl cyclic silanone was proposed as chemical structure. However, the MS^2 mass spectrum cannot confirm this exact structure but this molecule is strongly envisaged.

(5-b) (cyclosiloxanyl)ether (n<Si5)

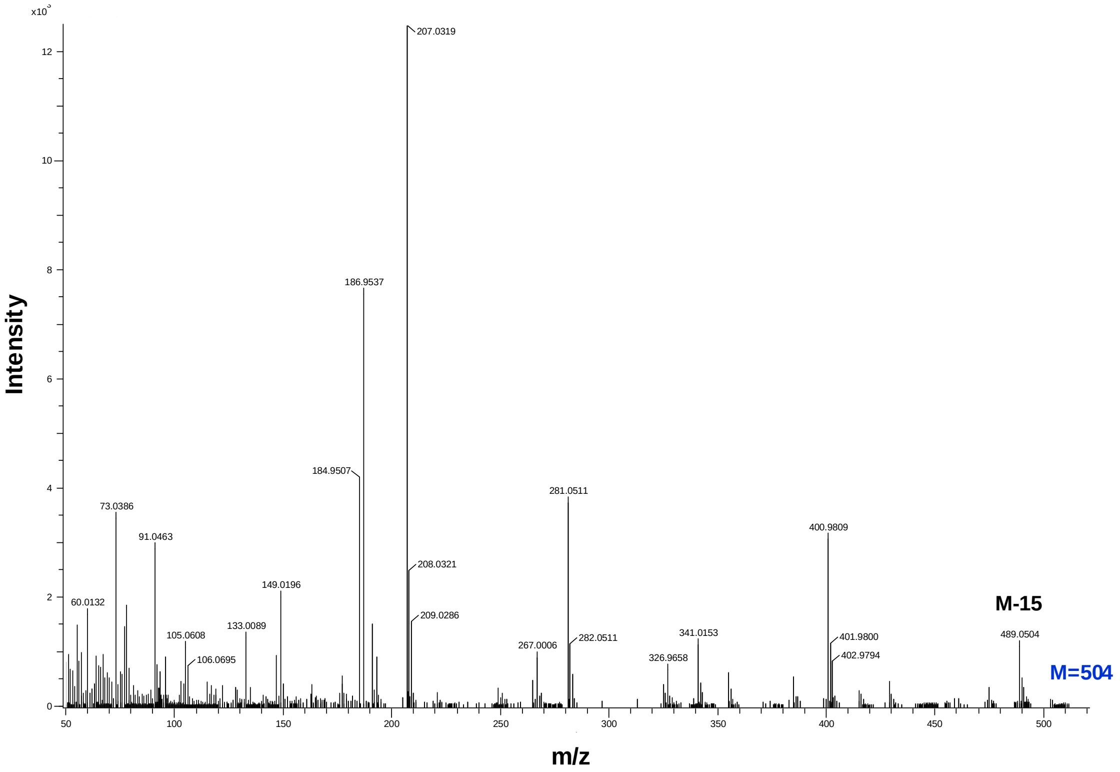


Figure A 20. EI mass spectrum of (pentamethylcyclotrisiloxanyl)heptamethylcyclotetrasiloxanyl ether ($C_{12}H_{36}O_8Si_7$) obtained for the test B by GC/TOFMS

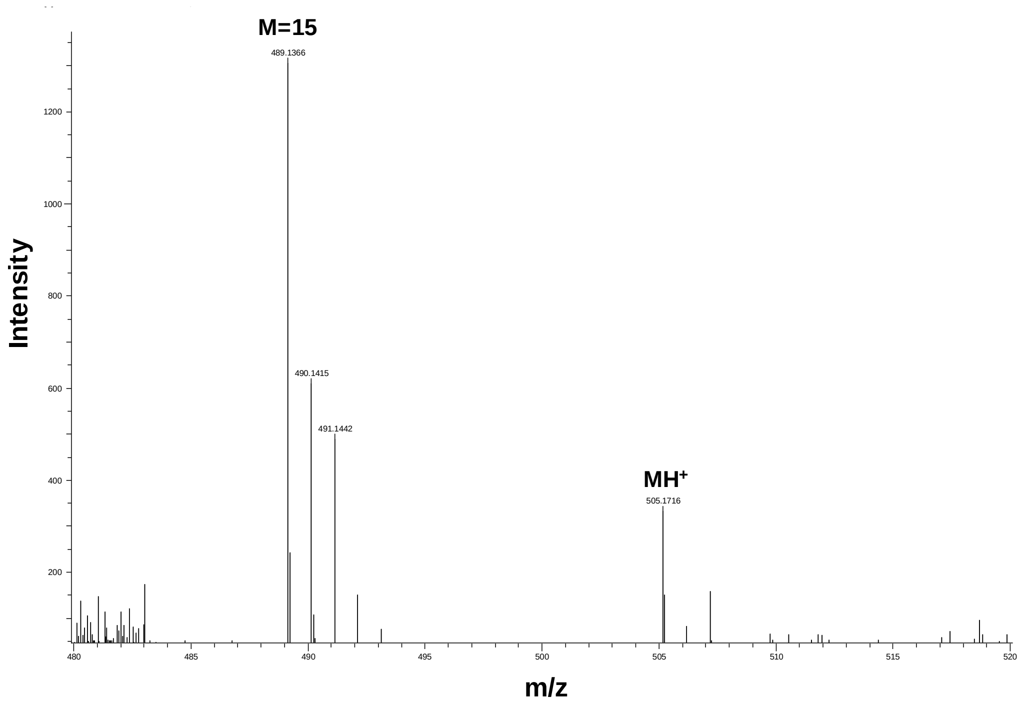


Figure A 21. mass spectrum of (pentamethylcyclotrisiloxanyl)heptamethylcyclotetrasiloxanyl ether ($C_{12}H_{36}O_8Si_7$) obtained for the test B by GC/TOFMS

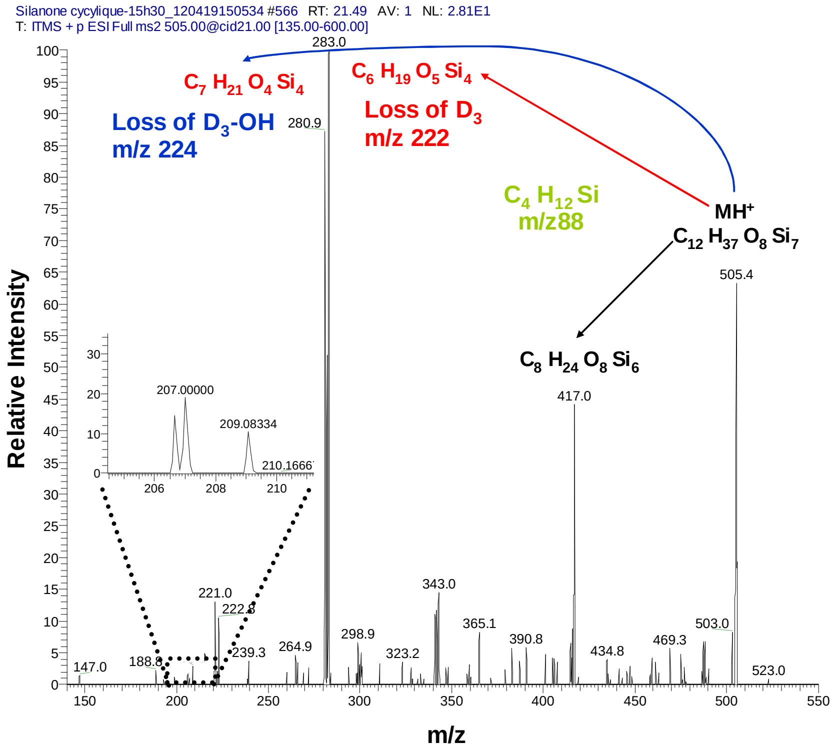
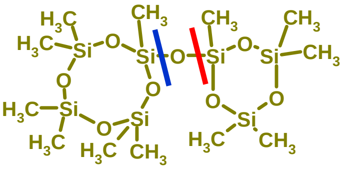


Figure A 22. MS^2 spectrum of pentamethylcyclotrisiloxanyl)heptamethylcyclotetrasiloxanyl ether ($C_{12}H_{36}O_8Si_7$) using ESI/MS

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_{12}H_{36}O_8Si_7$	2	504	505/489	489/401/355/281	

Validation

The FT-ICR/MS analysis demonstrated that the $C_{12}H_{36}O_8Si_7$ molecule has two unsaturations in its chemical structure. Thanks to the GC/TOFMS in CI mode (Figure A21), this molecule was characterized by its retention time and also by its EI mass spectrum (Figure A20). Similarly to $C_6H_{19}O_5Si_4$ (Si_4), a M-15 peak at m/z 489 indicated the loss of CH_3. According to the DBE of 2 and to the raw formula $C_{12}H_{36}O_8Si_7$, a second chemical structure was possible for this raw formula. This structure was possible for a number of Si above 5 because of the stability of the cyclic siloxane. This chemical structure was clearly strengthened by MS^2 (Figure A22). The scission of the O-Si-O bond was demonstrated and could occur by two pathways. The first one (in blue) was characterized by the detection of $C_7H_{21}O_4Si_4$ at m/z 281 with a loss of D_3-OH (m/z 224). The second one (in red) was established by the detection of $C_6H_{19}O_5Si_4$ at m/z 283 with a loss of D_3 (m/z 222) allowed by a rearrangement of the CH_3. Thus, this chemical structure was strengthened. The characterization of the others compounds of the family was achieved thanks to the repetition pattern C_2H_6OSi using the exact mass in FT-ICR/MS or using the retention times by GC/TOFMS.

(6) α-hydroxy,ω-methyl polysiloxanes

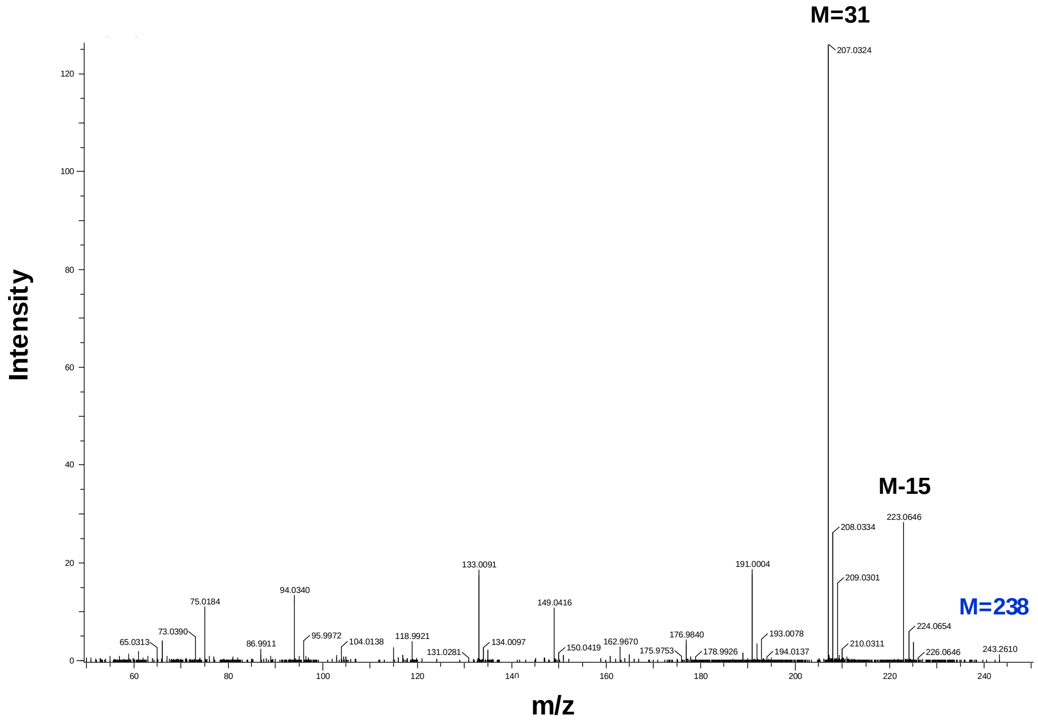


Figure A 23. EI mass spectrum of heptamethyltrisiloxanol obtained for the test B by GC/TOFMS

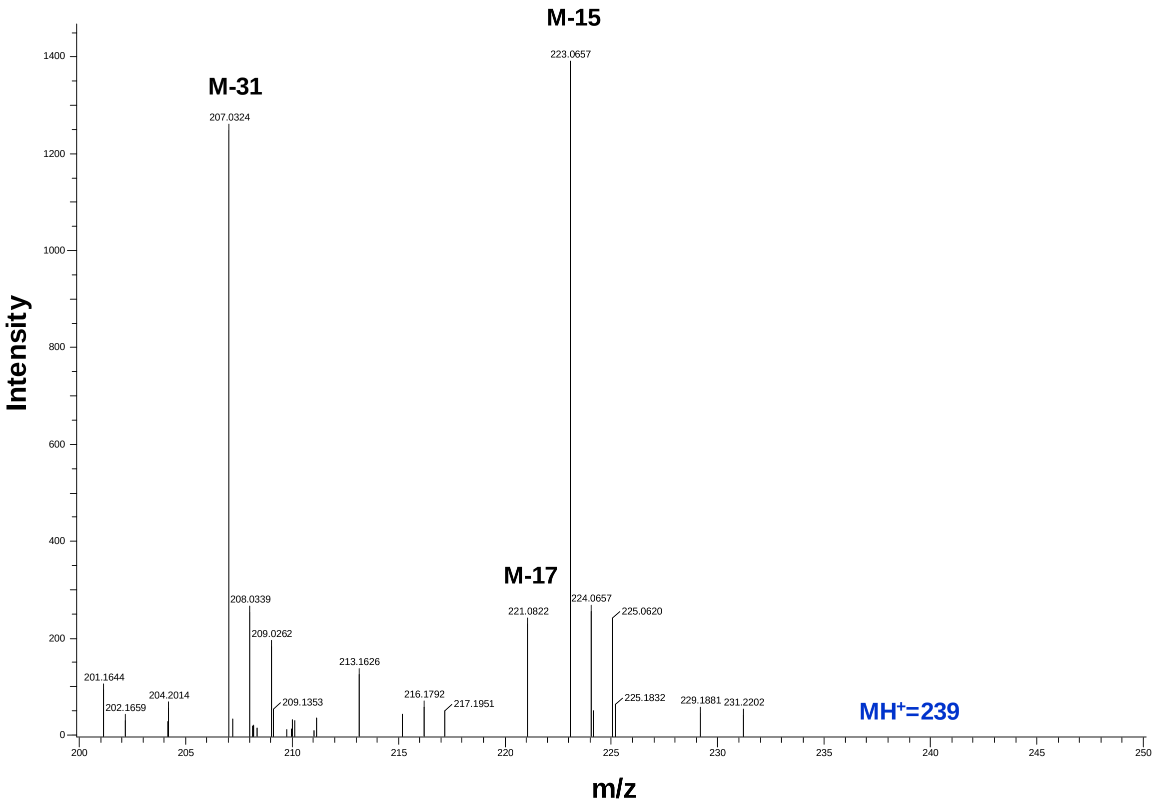


Figure A 24. CI mass spectrum of heptamethyltrisiloxanol obtained for the test B by GC/TOFMS

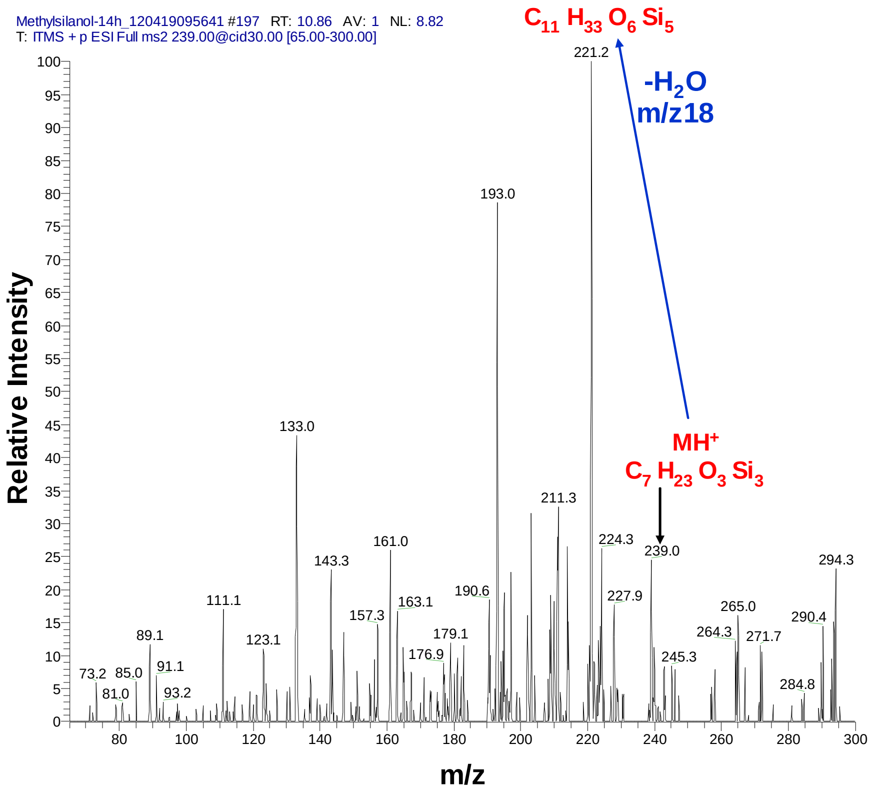
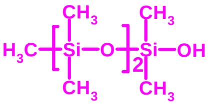


Figure A 25. MS^2 mass spectrum of heptamethyltrisiloxanol ($C_7H_{22}O_3Si_3$) using ESI/MS

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_7H_{22}O_3Si_3$	0	238	223/221/207	223/207/191	

Validation

The FT-ICR/MS analysis demonstrated that the $C_7H_{22}O_3Si_3$ molecule has no unsaturation in its chemical structure. Thus, this structure appeared as linear but with one more oxygen group than octamethyltrisiloxane (L_3) previously characterized. Thanks to the detection of the M-15 and M-17 peaks, respectively at m/z 223 and m/z 221 in the GC/TOFMS in CI mode (Figure A24), the loss of CH_4 and H_2O was confirmed. Thus, the heptamethyltrisiloxanol ($C_7H_{22}O_3Si_3$) was proposed. Even if the sensitivity was not excellent, this chemical structure was strengthened by the MS^2 spectrum (Figure A25) with the loss of water from the protonated molecule. The characterization of the others compounds of the family was achieved thanks to the repetition pattern C_2H_6OSi using the exact mass in FT-ICR/MS or using the retention times by GC/TOFMS.

(7-a) Methyl hydroperoxy cyclic siloxane

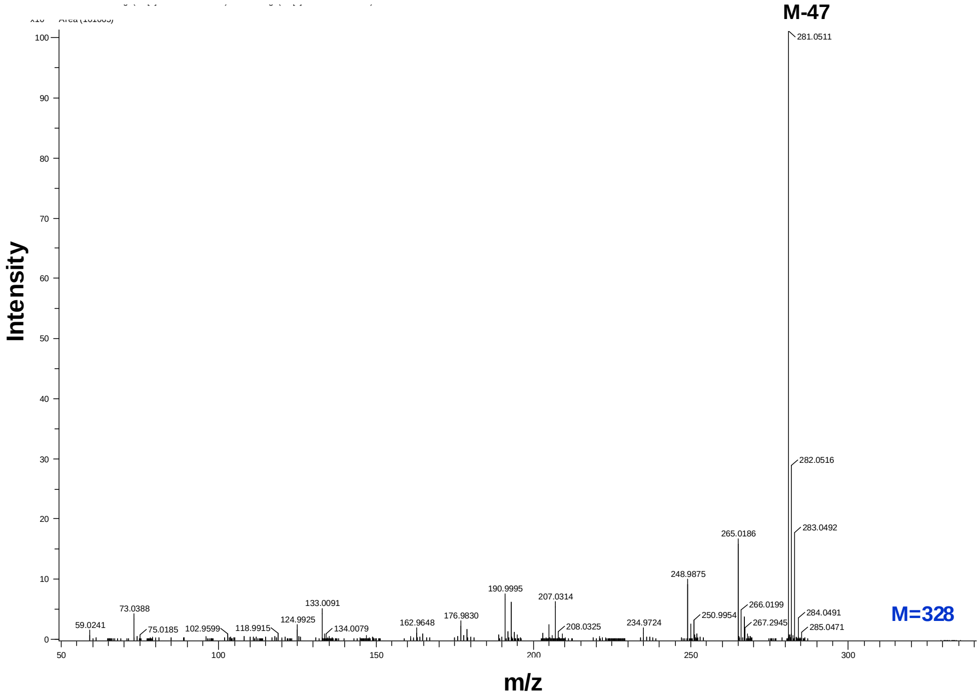


Figure A 26. EI mass spectrum of heptamethyl(hydroperoxymethyl)cyclotetrasiloxane obtained for the test B by GC/TOFMS

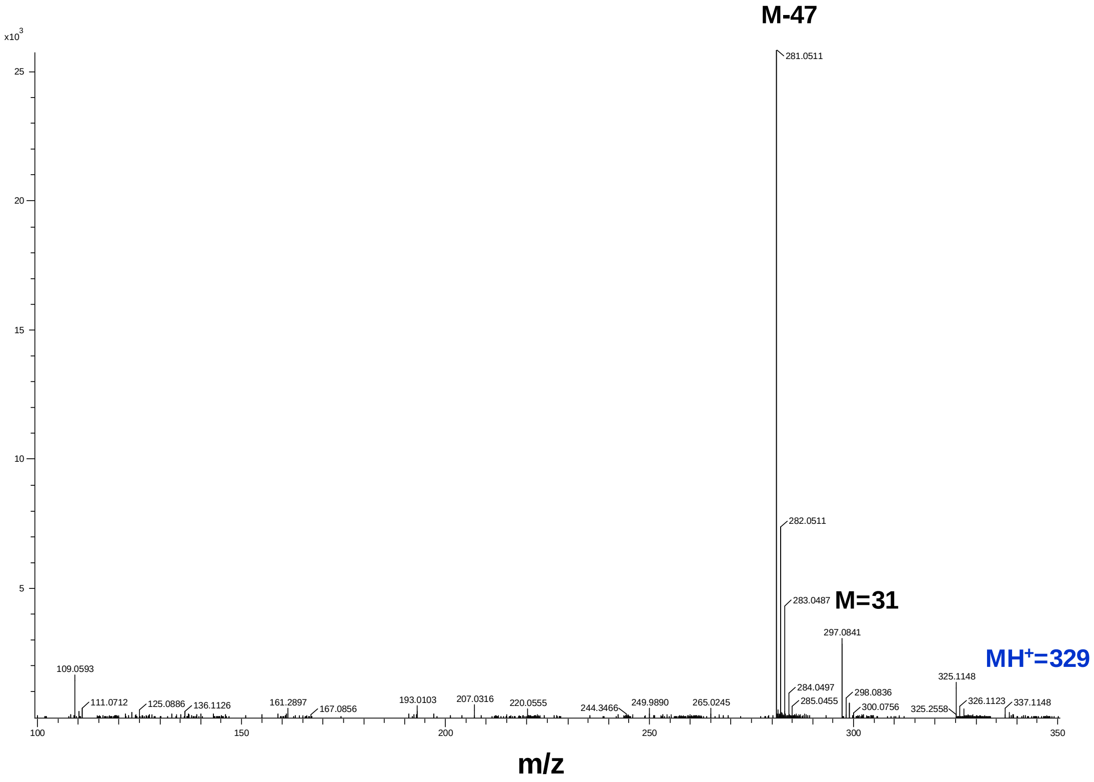


Figure A 27. CI mass spectrum of heptamethyl(hydroperoxymethyl)cyclotetrasiloxane obtained for the test B by GC/TOFMS

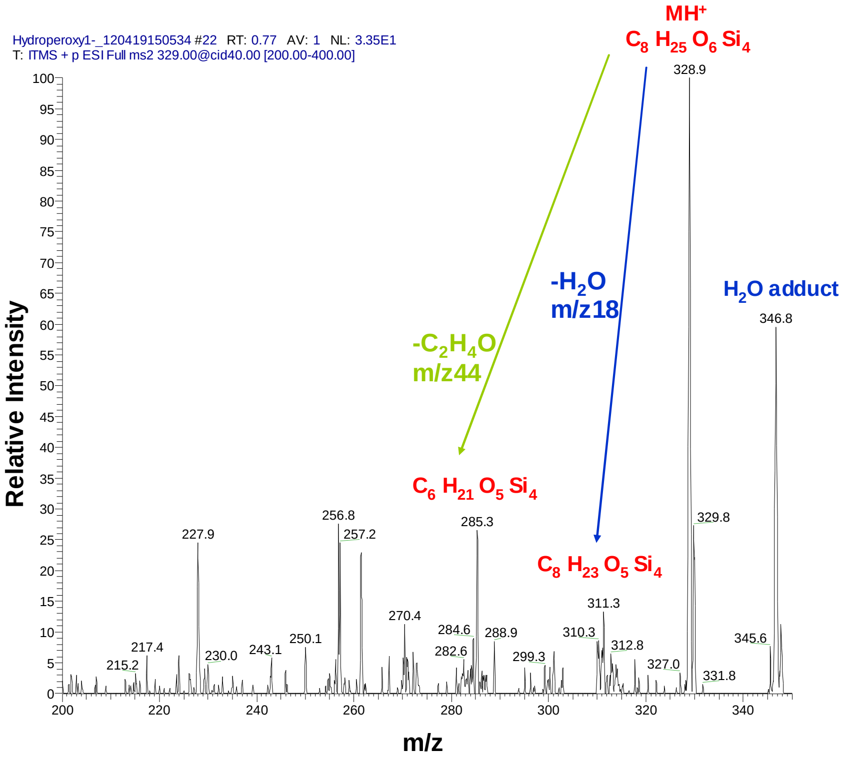
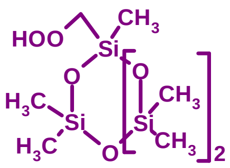


Figure A 28. MS^2 mass spectrum of heptamethyl(hydroperoxymethyl)cyclotetrasiloxane ($C_8H_{25}O_6Si_4$) using ESI/MS

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_8 H_{24} O_6 Si_4$	1	328	325/297/281	281/265/249/207/191	

Validation

The FT-ICR/MS analysis demonstrated that the $C_8 H_{24} O_6 Si_4$ molecule has 1 unsaturation in its chemical structure. Thus, this structure appeared as cyclic because it was more stable that a double bond. Sommerlade *et al.* [107] have previously characterized heptamethyl (hydroperoxymethyl) cyclotetrasiloxane ($C_8H_{25}O_6Si_4$) by its EI fragments ions. These ions are similar to the ions detected in our EI mass spectrum (Figure A26) with the major peak M-47 at m/z 281 perfectly fitted to the loss of CH_2OOH. The molecular mass of this compound was not conserved in CI mode (Figure A27). Despite the low concentration of this compound, the MS^2 spectrum confirmed the presence of OH group by the elimination of water from the protonated molecule at m/z 311 (Figure A28). This group was also observed by Sommerlade *et al.* [107]. The characterization of the others compounds of the family was achieved thanks to the repetition pattern C_2H_6OSi using the exact mass in FT-ICR/MS or using the retention times by GC/TOFMS.

(7-b) Propyl hydroperoxy cyclic siloxane

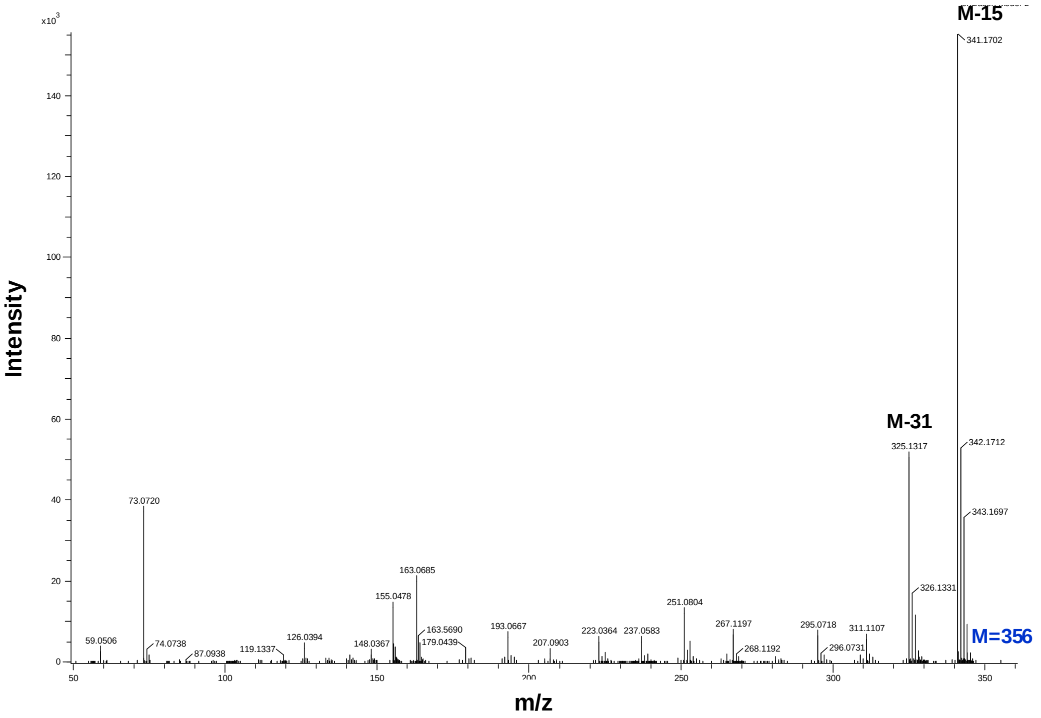


Figure A 29. EI mass spectrum of $C_{10}H_{28}O_6Si_4$ obtained for the test B by GC/TOFMS

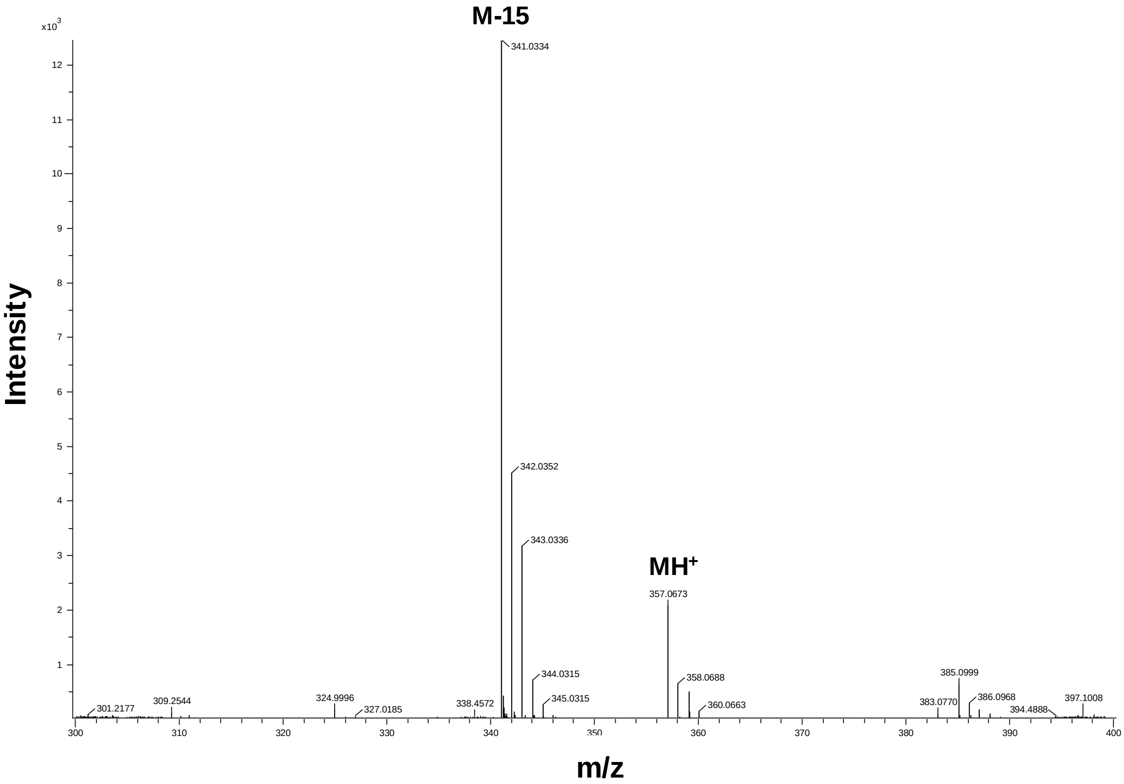
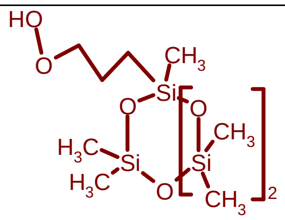


Figure A 30. CI mass spectrum of $C_{10}H_{28}O_6Si_4$ obtained for the test B by GC/TOFMS

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_{10}H_{28}O_6Si_4$	1	356	not detected	341/325/251/163/155/73	

Validation

The FT-ICR/MS analysis demonstrated that the $C_{10}H_{28}O_6Si_4$ molecule has also 1 unsaturation in its chemical structure similarly to the previous molecule ($C_8H_{24}O_6Si_4$) (7-a). The EI and CI mass spectra just allowed to confirm the loss of CH_4. (Figure A29 and Figure A30). Due to the low intensity signal of this species, the MS^2 experiments cannot be strengthened this structure. The characterization of the others compounds of the family was achieved thanks to the repetition pattern C_2H_6OSi using the exact mass in FT-ICR/MS or using the retention times by GC/TOFMS.

(8) Sylene cyclic siloxanes

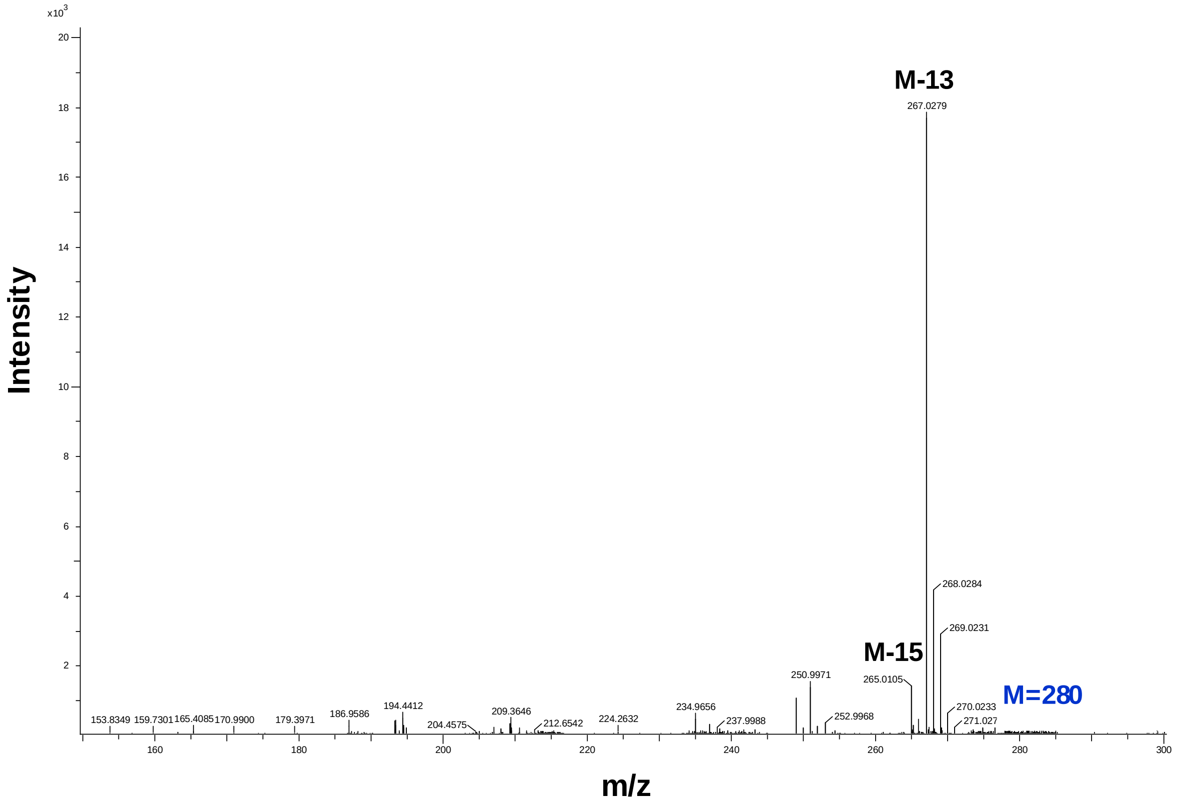


Figure A 31. S EI mass spectrum of obtained for $C_7H_{20}O_4Si_4$ the test B by GC/TOFMS

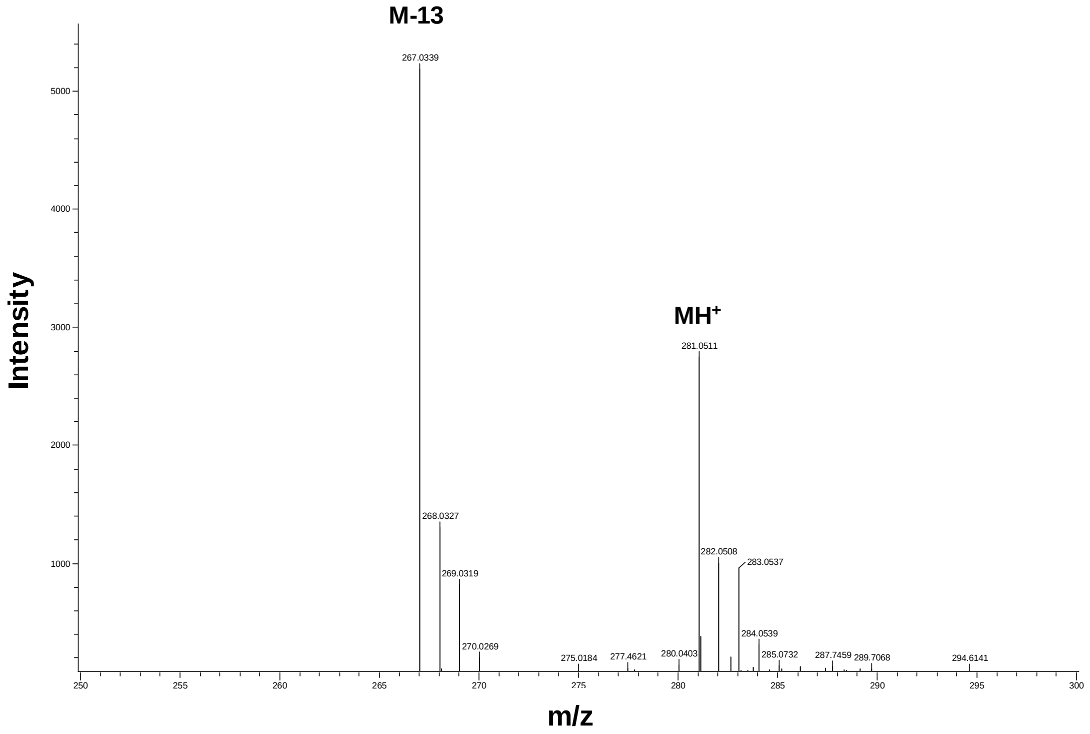
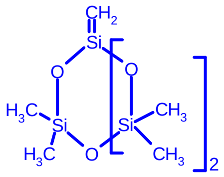
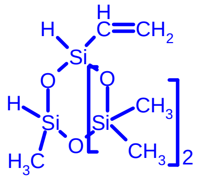
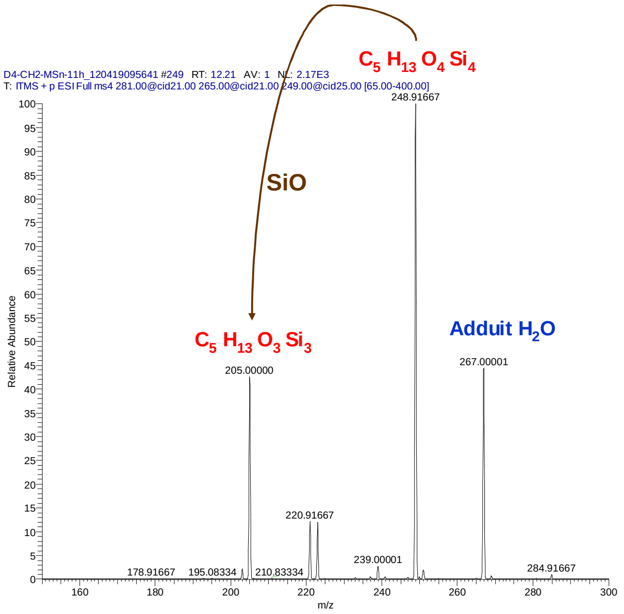


Figure A 32. CI mass spectrum of obtained for $C_7H_{20}O_4Si_4$ the test B by GC/TOFMS

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_7 H_{20} O_4 Si_4$	2	280	281/267	267/265/251/249/235/207/191	 



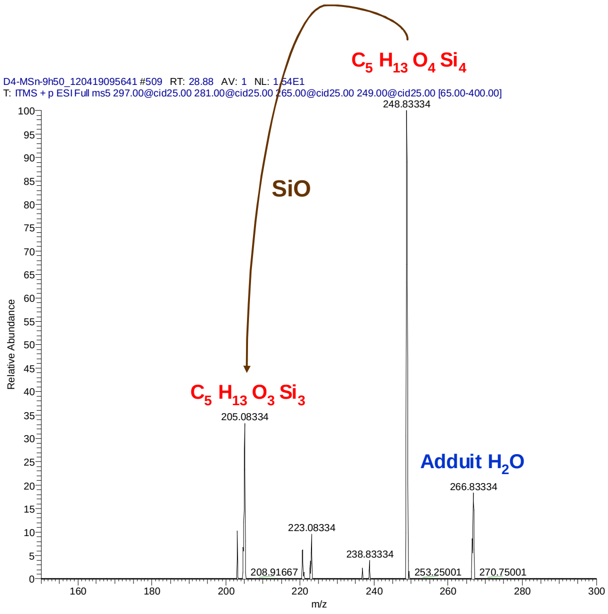


Figure A 33. MS^4 mass spectrum of $C_7 H_{20} O_4 Si_4$ using ESI/MS

Figure A 34. MS^5 mass spectrum of $C_8 H_{24} O_4 Si_4$ using ESI/MS

Validation

The FT-ICR/MS analysis demonstrated that the $C_7 H_{20} O_4 Si_4$ molecule has 2 unsaturations in its chemical structure. The CI mass spectrum allowed to confirm the presence of this molecule under its protonated form at m/z 281 by GC/TOFMS (Figure A32). The GC/TOFMS analysis provided information about the fragmentation of this species using its EI mass spectrum (Figure A31). The major ion in this EI mass spectrum at m/z 267 matches to the M-13 peak. The M-15 peak at m/z 265 was also detected but with a low intensity and fitted with the loss of CH_3. According to the first compound of the family detected with three Si atoms, a DBE of 2 and the raw formula $C_5H_{14}O_3Si_3$, two chemical structures were proposed. Using the same repetition pattern C_2H_6Osi, the Si_4 structures were indicated in the Table.

Experiments up to MS^4 was performed on this Si_4 molecule (Figure A33) and compared to the MS^5 achieved on D_4 ($C_8H_{24}O_4Si_4$) (Figure A34). These mass spectra were similar and the comparison did not allow to distinguish a difference in the fragmentation of these two molecules. These experiments did not confirm the chemical structure of $C_7H_{20}O_4Si_4$ but allowed to eliminate the second proposed structure with Si-CH=CH_2 and Si-H bonds (Figure A34). Indeed, the scission of these Si-H bonds were not observed using MS^2 for $C_7H_{20}O_4Si_4$. Similarly to D_4, only the loss of CH_4 from the protonated molecule was observed for this structure. The CI mass spectrum showed a major peak fitted to a mass difference of 14 (CH_2) from the protonated molecule (MH^+) (Figure A32). The EI mass spectrum also showed the detection of a major ion fitted to M-13 peak from the molecular mass (Figure A31). Thus, the first chemical structure (Si=CH_2) cannot be totally strengthened by MS^2 but it was strongly possible thanks to the GC/TOFMS mass spectra.

The characterization of the others compounds of the family was achieved thanks to the repetition pattern C_2H_6OSi using the exact mass in FT-ICR/MS or using the retention times by GC/TOFMS.

(9) Dimethoxy polysiloxanes

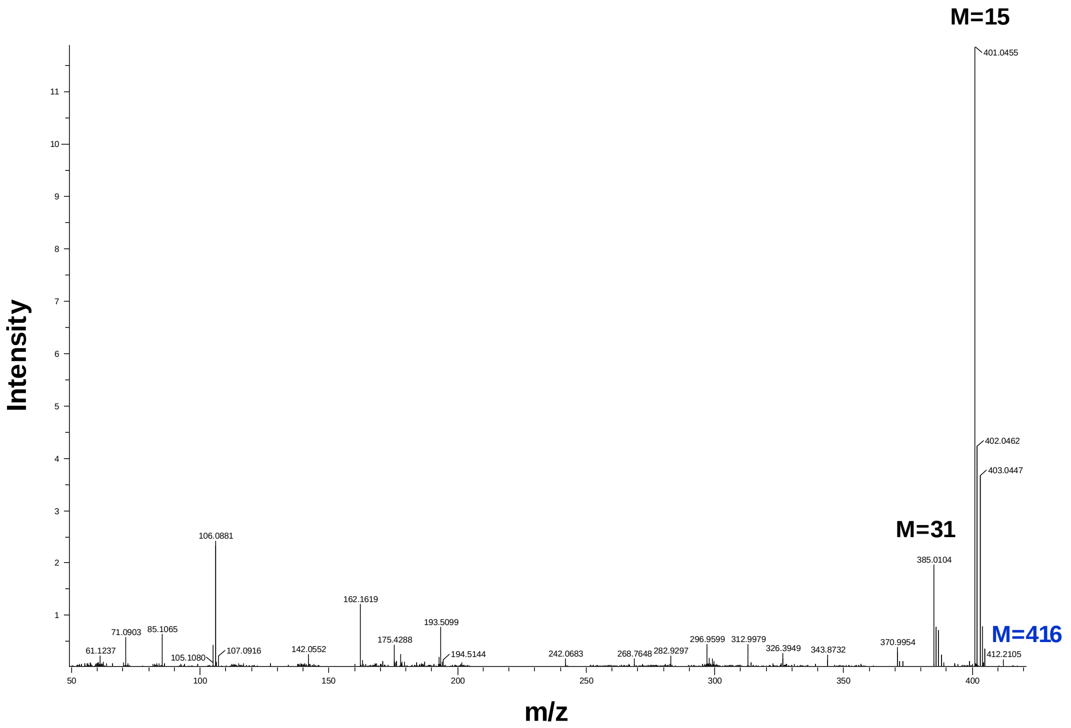


Figure A 35. EI mass spectrum of dimethoxydecamethylsilane ($C_{12}H_{36}O_6Si_5$) obtained for the test B by GC/TOFMS

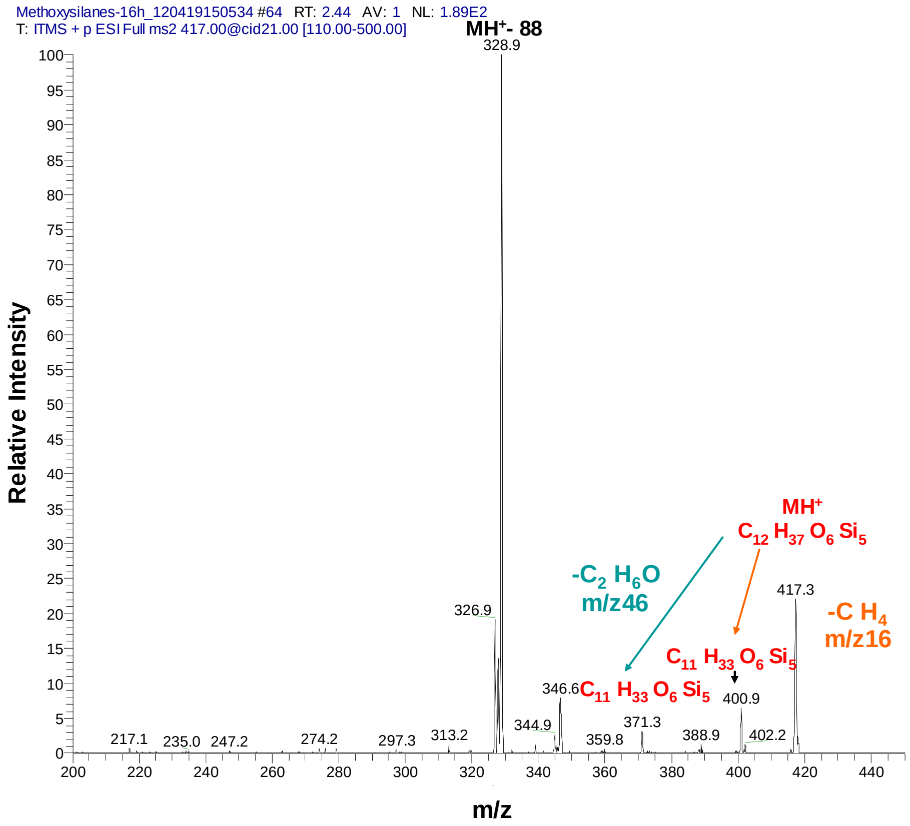
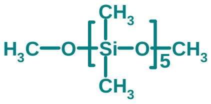


Figure A 36. MS^2 mass spectrum of dimethoxydecamethylsilane ($C_{12}H_{36}O_6Si_5$) using ESI/MS

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_{12}H_{36}O_6Si_5$	0	416	not detected	401/385/371	 $H_3C-O-[Si(CH_3)_2-O]_5-CH_3$

Validation

The identification of this molecule is illustrated because the intensity of the Si_5 compound is more important than the Si_4 molecule. The FT-ICR/MS analysis demonstrated that the $C_{12}H_{36}O_6Si_5$ molecule has no unsaturation in its chemical structure and appeared as linear. According to the raw formula, the DBE and the C_2H_6OSi pattern, dimethoxysilanes structure was proposed for this family. The low concentration of this molecule did not allow the acquisition of the CI mass spectrum. The EI mass spectrum demonstrated the presence of two main peaks M-15 at m/z 401 and M-31 at m/z 385 previously discussed for the (1) cyclic siloxane (D_n) (Figure A7). These results cannot confirm the proposed structure.

The MS^2 spectrum demonstrated the presence of ions at m/z 401 (M-16) and m/z 371 (M-46), respectively fitted to the loss of CH_4 and C_2H_6O from the protonated molecule (m/z 417) (Figure A36). The second methoxy group proposed based on the raw formula was present but this group was not necessarily present on the end group of the linear chain.

The characterization of the others compounds of the family was achieved thanks to the repetition pattern C_2H_6OSi using the exact mass in FT-ICR/MS or using the retention times by GC/TOFMS.

(10) Methylpropyl cyclic siloxanes

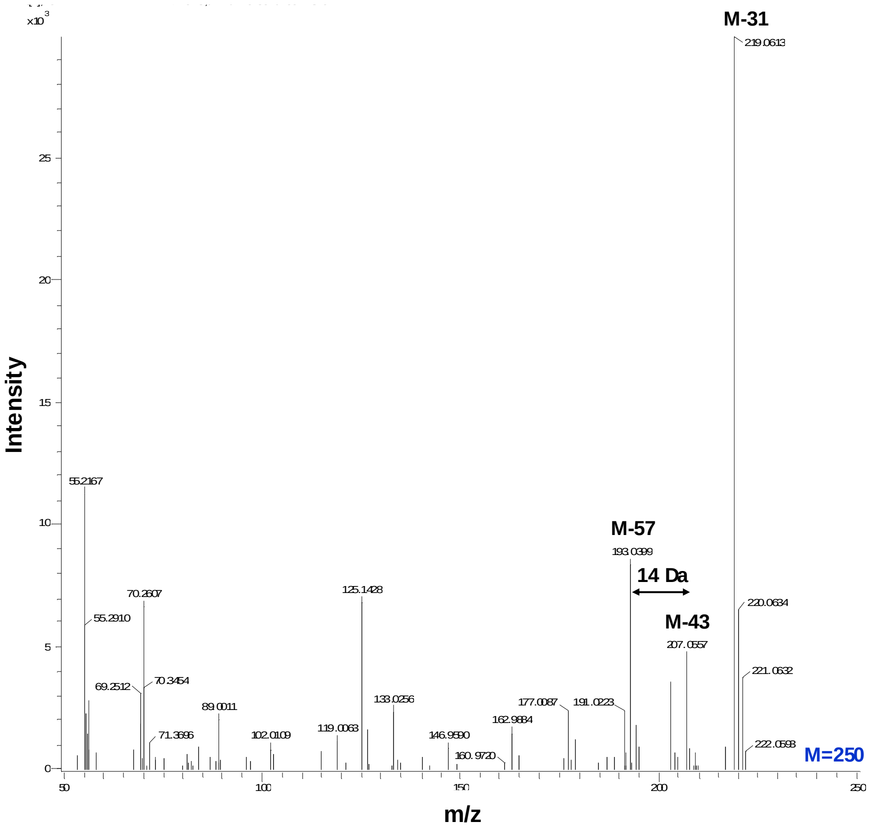


Figure A 37. EI mass spectrum of $C_{18}H_{22}O_3Si_3$ obtained for the test B by GC/TOFMS

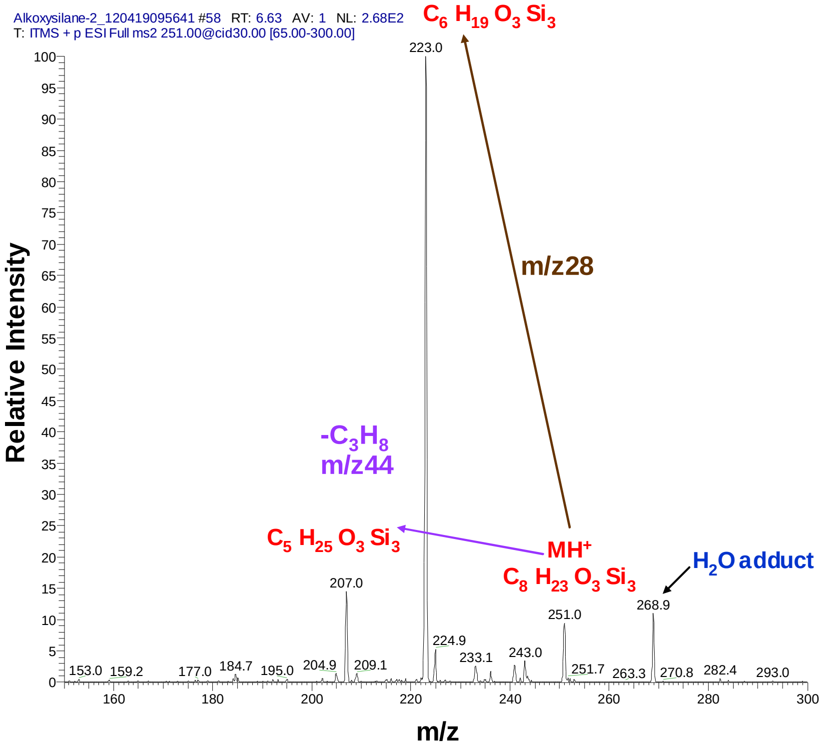
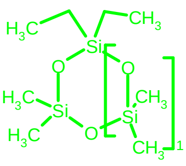
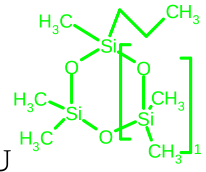


Figure A 38. MS^2 mass spectrum of $C_{18}H_{22}O_3Si_3$ using ESI/MS

Raw formula	DBE	Molecular mass (g/mol)	Ions (CI)	Ions (EI)	Chemical structure
$C_8H_{22}O_3Si_3$	1	250	not detected	219/207/193/163	 OU 

Validation

The identification of this molecule is illustrated because the intensity of the Si_3 compound is more important than the Si_4 molecules. The FT-ICR/MS analysis demonstrated that the $C_8H_{22}O_3Si_3$ molecule has 1 unsaturation. The EI mass spectrum indicated two ions at m/z 219 (M-31) and m/z 207 (M-43), respectively matched to the scission of 2 Si-CH_3 with the elimination of CH_4 (previously discussed for D_n) and to the loss of C_3H_7 (m/z 43) (Figure A37). These results allowed to eliminate the first chemical structure because the loss of C_2H_5 (m/z 29) was not observed.

MS^2 experiments clearly strengthened this chemical structure by the detection of the fragment ion at m/z 207 perfectly fitted to the loss of C_3H_8 (m/z 44) from the protonated molecule (m/z 251) (Figure A38). However, the ion fragment at m/z 223 fitted to the loss of m/z 28 from the protonated molecule cannot be explained.

The characterization of the others compounds of the family was achieved thanks to the repetition pattern C_2H_6OSi using the exact mass in FT-ICR/MS or using the retention times by GC/TOFMS.