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Optimization of platinum-based silicone’s hydrosilylation for hose manufacturing

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Directed by	Dr. Salvador Borrós Gómez Dra. Núria Agullo Chaler Dr. David Sánchez Garcia.

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Summary.

Platinum-cured silicones for the sanitary field are subject to very strict regulations to ensure an extremely low level of both volatile and extractable compounds migrated from the elastomeric product. As a result, the processing of silicone rubber has always included a post-curing final step. In addition, this additional step is generally thought to improve the physical characteristics of platinum-cured silicones by driving the cure up to completion. However, post-curing entails a significant increase in time and money in silicone rubber's manufacturing process, so many manufacturers have looked for alternatives to eliminate the need to post-cure materials after curing.

Another problem related to silicone rubber's productivity is that to process the silicone elastomer at lower cost, achieving a platinum catalyst with a reasonable shelf-life is required. Currently, the most widely used in the silicone industry is the Karstedt's catalyst; however, its reactivity is limited due to the rapidly dissociation of Pt-(μ-η^4-dvtms) coordination bonds, forming platinum metal colloids.

The present work attempts to address these productivity issues by focusing on the development of an own catalyst technology, that can be prepared with a lower or comparable cost to that of commercial catalysts.

Finally, with the aim of rethinking the usefulness of post-curing, volatiles and extractables migrated from the silicone rubber cured with a commercial catalyst are analyzed and compared to the ones evolved when using the developed catalyst.

Resum.

La silicona curada amb platí destinada al sector sanitari està subjecta a normatives molt estrictes amb la finalitat d'assegurar un molt baix contingut de compostos volàtils o extraïbles; per això, el procés de fabricació sempre ha inclòs un pas final de post-curat. Aquest procés addicional, ja que impulsa el curat fins a la seva finalització, es considera que millora també les característiques físiques dels elastòmers. No obstant això, comporta un important increment de temps i diners en la producció del cautxú de silicona, per la qual cosa molts fabricants han buscat alternatives a aquesta etapa addicional.

Un altre problema relacionat amb la productivitat és que, per a poder processar l'elastòmer de silicona a menor cost, és necessari tenir un catalitzador de platí amb una vida útil raonable. Actualment el més utilitzat en la indústria és el catalitzador de Karstedt; però, la reactivitat d'aquest catalitzador està limitada per la ràpida dissociació dels enllaços de coordinació Pt-(μ-η^4-dvtms), formant platí col·loidal.

En aquest treball s'intenta abordar aquests problemes de productivitat centrant-se en el desenvolupament d'un catalitzador de tecnologia pròpia, la producció del qual suposi un cost menor o equiparable als catalitzadors comercials.

Finalment, amb la finalitat de replantejar la utilitat del procés de post-curat, s'analitzen els volàtils i extraïbles que migren des del material durant aquest procés, comparant la silicona curada amb un catalitzador comercial i l'obtinguda amb el de tecnologia pròpia.

Resumen.

La silicona curada con platino destinada al sector sanitario está sujeta a normativas muy estrictas con el fin de asegurar un muy bajo contenido de compuestos volátiles o extraíbles; por ello, el proceso de fabricación siempre ha incluido un paso final de post-curado. Este proceso adicional, puesto que impulsa el curado hasta su finalización, se considera que mejora también las características físicas de los elastómeros. No obstante, conlleva un importante incremento de tiempo y dinero en la producción del caucho de silicona, por lo que muchos fabricantes han buscado alternativas a esta etapa adicional.

Otro problema relacionado con la productividad es que, para poder procesar el elastómero de silicona a menor coste, es necesario tener un catalizador de platino con una vida útil razonable. Actualmente el más utilizado en la industria es el catalizador de Karstedt; sin embargo, la reactividad de este catalizador está limitada por la rápida disociación de los enlaces de coordinación Pt-(μ-η^4-dvtms), formando platino coloidal.

En este trabajo se intenta abordar estos problemas de productividad centrándose en el desarrollo de un catalizador de tecnología propia, cuya producción suponga un coste menor o equiparable a los catalizadores comerciales.

Finalmente, con el fin de replantear la utilidad del proceso de post-curado, se analizan los volátiles y extraíbles que migran desde el material durante este proceso, comparando la silicona curada con un catalizador comercial y la obtenida con el de tecnología propia.

Glossary of terms, abbreviations and acronyms.

$(M)^+$: Molecular ion
$|\eta^*|$: Complex viscosity
2RMM: Two-roll rubber mixing mill
Å: Ångström
ANOVA: Analysis of variance
AROP: Anionic ring-opening polymerization
BfR: Bundesinstitut für Risikobewertung
CFR: Code of Federeal Regulations
CI: Confidence interval
cSt: Centistokes
D_4: Octamethyl-cyclotetrasiloxane
Da: Dalton or unified atomic mass unit
DAS: Diallyl sulfide
df: Degrees of freedom
DSC: Differential scanning calorimetry
DTG: First derivative thermogravimetric curve
dvtms: 1,1,3,3-tetramethyl-1,3-divinyl-disiloxane
$\mathbf{E_a}$: Activation energy
EC: European Commission
FCM: Food Contact Materials
FDA: Food and Drug Administration
F-test: Critical value of the F-distribution
G': Elastic modulus
G'': Viscous modulus
G^*: Complex shear modulus
GMP: Good manufacturing practices
HCR: High consistency silicone rubber
HTV: Hight Temperature Vulcanisation
Hz: Herzt
ICP-AES: Inductively coupled plasma atomic emission spectrometry
ID: Inner diameter
in: Inch
IR: Polyisoprene Rubber
IRHD: International Rubber Hardness Degrees
IIR: Butyl Rubber
kN: Kilonewton
m: Slope
$M \pm SD$: M: Mean, SD: standard error
$MgSO_4$: Magnesium sulfate
MPa: Megapascal
MS: Mean square
NHC: N-heterocyclic carbenes
NIST: National Institute of Standards and Technology
NR: Natural Rubber
Olefin: unsaturated hydrocarbons, alkene,
PE: Polyethylene
PCBs: Polychlorinated biphenyls
PDMS: Polydimethylsiloxane
phr: Parts per Hundred Rubber
ppm: Parts per million
PTFE: Polytetrafluoroethylene
p-value: Level of statistical significance
PVC: Polyvinyl chloride
r^2: Goodness-of-fit measure for the linear regression model
RT: Retention time
RTV: Room Temperature Vulcanisation
SBS: Styrene-butadiene-styrene
SiO_2 gel: Silica gel
SiOC: Silicon oxycarbide
TC: Cure time
TEY: Total extractive yield
TGA: Thermogravimetric analysis
TOF: Turnover frequency
TON: Turnover number
$\mathbf{T_p}$: Peak temperature
$\mathbf{T_{room}}$: Room temperature
v: Volum

V_4**:** Tetravinyltetramethyl-cyclotetrasiloxane

VMQ**:** Vinyl-methyl-polysiloxane

w: Weight

α: Refers to the extent of conversion of the reactant to products

β: Heating rate

β atom**:** Refers to the second carbon atom that attaches to a functional group

$\rho_{23°C}$: Density at 23 °C

σ_{max}: Ultimate tensile strength

ω: Frequency

ε_{max}: Elongation at break

Table of contents.

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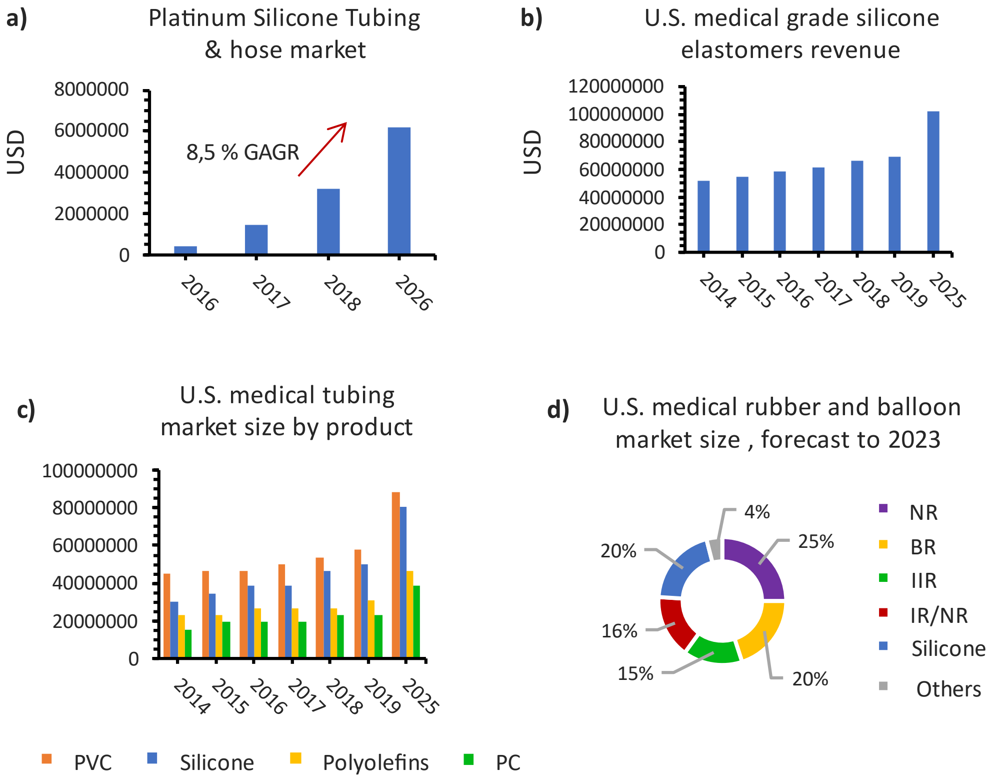
Chapter 1: Introduction.

1.1. Background.

This PhD project is focused on sanitary flexible tubing; that is tubing made from platinum-cured medical grade and food grade silicone rubber.

Platinum-cured silicone tubing has been valued by the global market at 3,230.8 million US$ in 2018, and it is expected to reach the 6,211.4 million by 2026 at a compound annual grow rate (CAGR) of 8.5 % (Figure 1.1, a). [1]



[Figure 1.1]: Medical silicone rubber's current market trends.[2]

The main factors which are accentuating this growth are the increasing adoption of minimally invasive medical procedures and the rising demand for medical tubing devices (Figure 1.1, c-d).

Not surprisingly, the excellent electrical insulating as well as biocompatibility properties shown by silicone rubber (Figure 1.2) have given rise to be one of the preferred raw material for being used in short-term implants and medical equipment; [3] as it offers a superior lot-to-lot consistency than latex, not to mention the concerns regarding allergic reactions in latex-sensitive individuals; as it is more inert than PVC, and when it is compared with most thermoplastic elastomers, silicone's enhanced chemical and thermal resilience provides more options for sterilization.

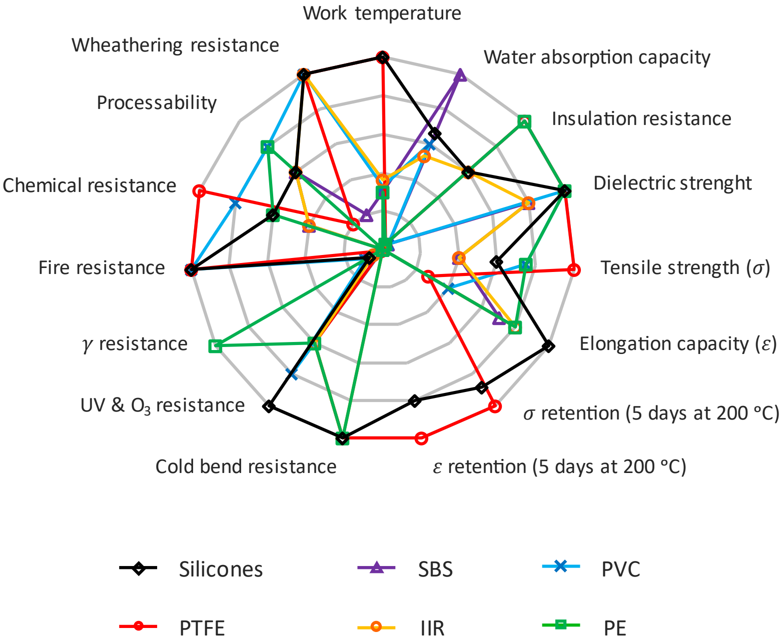
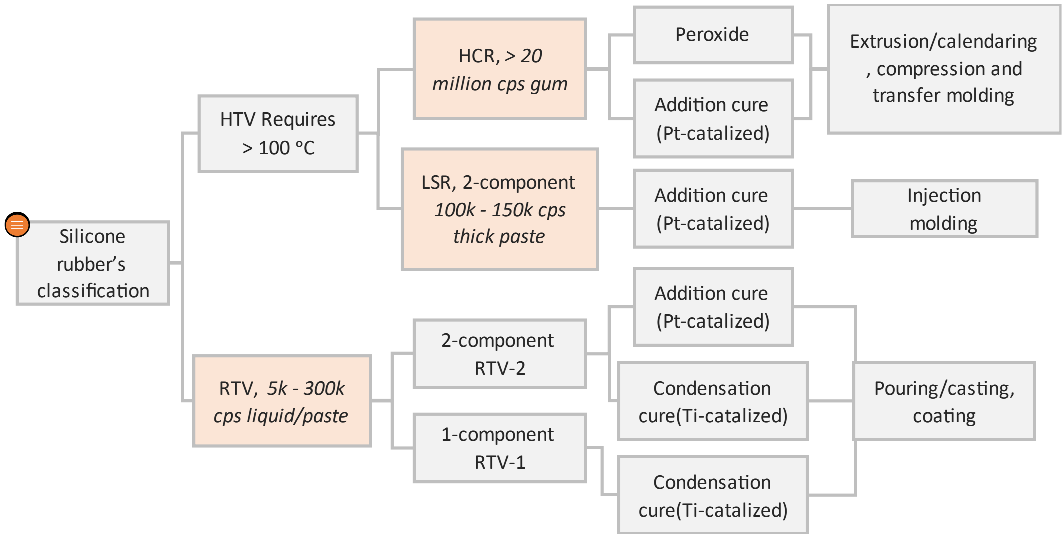


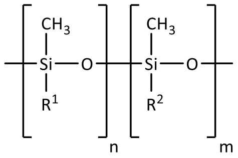
Figure 1.2]: Silicone rubber performance's comparison with other elastomers. [4]

Furthermore, they are also widely used to assist in pharmaceutical, food & beverage manufacturing and downstream processes. This is because hoses made of silicone are highly flexible, as well as enough resistant to kinking and tearing. [5] As a consequence, they offer a good choice for convey liquid, semi-liquid and even solid stuff at high temperatures or low pressures. In addition, they also withstand sudden high-pressure surges, or the repetitive movements of dosing and filling machines and it is able to absorb vibrations and compensate level differences when they are used in peristaltic pumps or at the outlets from tank hoppers and weighing tanks. Among all silicone rubber's types (Figure 1.3), the main raw material used for tubing applications is the high consistency silicone rubber (HCR), owing its putty-like consistency on its uncured state, which makes suitable this material for being processed into hoses through extrusion or mandrel-wrapped techniques.



[Figure 1.3]: Silicone rubber's classification according to the curing conditions, viscosity, used curing chemistry used and its method of processing.

HCR is a special type of hight temperature vulcanizing (HTV) silicone elastomer. It is made from silicone gums, i.e., straight polydimethylsiloxane's chains with very high molecular weight (300,000 to 700,000 Da) containing various reactive groups (Figure 1.4).



n=m and $R^1 = R^2$: CH_3; **MQ**, also known as PDSM-polydimethylsiloxane.

R^1: CH_3 and R^2: $-CH=CH_2$; **VMQ**, vinylmethyl- and dimethylsiloxane copolymer.

R^1: $-CH=CH_2$ and R^2: $-C_6H_5$; **PVMQ**, phenylmethyl-and VMQ copolymer.

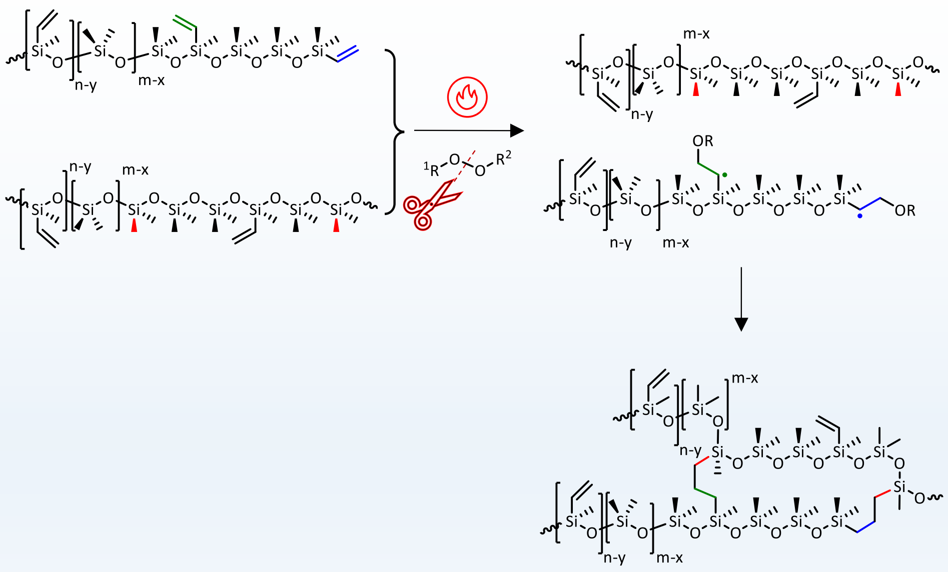
R^1: $-CH=CH_2$ and R^2: $-CH_2-CH_2-CF_3$; **FVMQ**, trifluoropropylmethyl- and VMQ copolymer.

[Figure 1.4]: General structure of HCR silicones and their classification according to DIN ISO 1629.

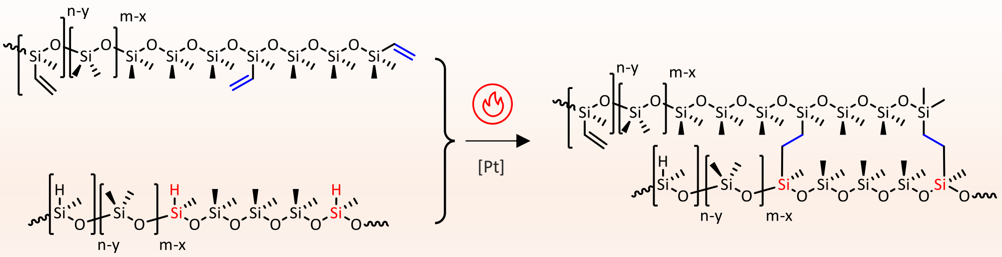
For sanitary tubing applications, the most frequently used are those containing geminal and/or terminal vinyl moieties, such as vinyl end-blocked VMQ or a combination of vinyl end-capped PDMS and VMQ polymers. [6–9]

These can be cross-linked using either organic peroxides in polycondensation systems (Figure 1.5, a) or platinum catalysts in polyaddition systems (Figure 1.5, b). [10] Free radical cure initiated by organic peroxides is the oldest and still most common chemistry used to cross-link elastomers. However, in the field of sanitary silicone tubing applications the preferred mechanism to be used today is the Pt cure, which it is also known as addition cure.

This is on account of the fact, that one of the most remarkable benefit of is this curing method, is that it does not split any PCBs' by-product, which might diffuse and concentrate at the surface, or even bloom leading to severe toxicological concerns. [3]



a) Peroxide-curing



b) Pt-catalysed Vi/H$^{\ominus}$ hydrosilylation reaction

[Figure 1.5]: Cross-linking mechanisms of vinyl-containing silicone rubbers.

The lack of such residues also gave rise to the reduction of the risk of mold fouling and hence, this reduces downtime for cleaning, and it improves the overall productivity. In addition, platinum curing includes an improved product clarity and consistency, and potentially somewhat better elongation, tensile strength, and tear strength.

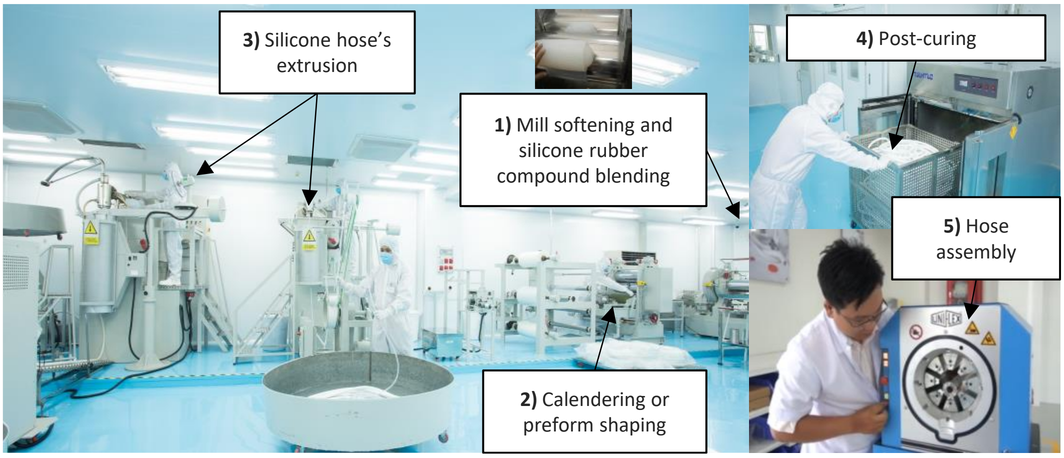
This type of curing, however, has also some drawbacks such as:

- Reagents for Platinum curing formulations are more expensive, which drives up the initial operating costs (though this initial expense may be offset over time by gains in productivity).
- Platinum catalyst is also sensitive to contamination, and exposure to latex, sulfur, tin-cure silicone and other products will inhibit silicone's cure.

Prior to be processed and cured, gums are compounded with amorphous silica-based reinforcing fillers in order to achieve useful engineering properties, since cross-linked gum alone only produces tensile strengths of 1.0 MPa. The preferred to be used is fumed silica [11], whose purity assures excellent physical and insulating properties to the silicone rubber. In addition to the fumed silica, silica aerogels [12] and precipitated amorphous silicas [13, 14] may be used as well. These are added to the gum stock at a rate of about 10 to 50.0 weight % [15–18] to increase rubber's hardness and the uniformity of force among network chains, thus reducing early fracture of overextended chains. Indeed, silica-reinforced cross-linked silicone rubbers typically have tensile strength of around 10 MPa, i.e., a factor of ten higher than the one achieved by the pure polymer. [11]

The obtained stiffer silicone compound, referred to as base stock, can now be processed and blended with the curing agents using the standard rubber equipment. More specifically, medical and food grade platinum-cured silicone hoses are built in a class 8 ISO-certified cleanrooms (Figure 1.6), in accordance with GMP guideline, following the next 5 steps:

1. Mill softening and blending process.
2. Preform preparation.
3. Hose building.
4. Post-curing.
5. Hose assembly.



[Figure 1.6]: Medical and food & beverage grade silicone hose standard manufacturing process (Courtesy: Venair Ibérica S.A.).

Notwithstanding, although platinum-cured silicone tubing should be expected to result in low extractable and leachable levels compared to the peroxide-cured one; still in all it has been determined that between a 0.5 to 2.0 weight % [19] volatiles are easily outgassed from rubber articles. Therefore, when used in pharmaceutical, food-contact or healthcare applications platinum-cured silicone hoses must be post-cured in hot air circulating ovens as well, since otherwise, they could not be validated and used in such sensitive industrial areas.

Aside from the regulatory compliance, post-curing the platinum-cured silicone rubber it also done to improve the mechanical response of the rubber by driving the cure up to completion. [21,22] These changes in the mechanical properties can be very important in specific applications, as for e.g. when silicone hoses are used in peristaltic pumps it is required a low hysteresis to ensure the stability of the flow. [23] Post-curing may be also necessary for medical devices applications to improve silicone-to-silicone bonding [20], like for e.g., to assemble a silicone catheter shaft with a silicone balloon. Here any remaining low molecular weight fluid able to migrate to the surface, could be act as a release agent, negatively impacting into the adhesive's efficacy used for this assemble.

However, despite their feasible advantages, silicone rubber's post-cure is undoubtedly a highly cost endeavour, which it greatly decreases productivity and increases tubing's processing costs. As a result, platinum-cured silicone hose manufacturers are looking for ways to eliminate this additional cure step in order to cut the costs associated with it. It is in this context that an industrial PhD project was proposed to be done in collaboration with Venair Ibérica S.A.

1.2. Objectives.

The main objective of the present work consists of developing an own technology regarding the platinum-cured silicone, focusing mainly on the development of an in-house made catalyst. The obtained know-how will give the company a competitive advantage in the commercial area of sanitary platinum-cured silicone since it will enhance the control over the process. The synthetic procedure developed must be economically viable with the current resources of the company without implying significant increases on the process expenses.

Subsequently, the following secondary objectives will also be covered:

- Determine whether the new catalyst influences or not on the post-curing step.

- Exhaustive study over all the phenomena occurring during the post-curing process in order to rethink its usefulness.
- Once the post curing effects have been stablished, it will be necessary to present alternatives to post-curing with the objective of minimizing production costs.
- Optimizing the own technology catalyst regarding its reactivity and stability in order to guarantee a reasonable pot-life.

1.3. Outline of the PhD.

The present PhD will address this post-curing issue trying to bring some light to this step of the manufacturing process.

First of all, and taking into account that the need of post-curing might be due to a not efficient curing process, **Chapter 2** will be focused on the synthesis and scaling up of a platinum catalyst. Furthermore, this study will provide a valuable know-how for the company which will make it possible to gain control on its own production lines, regardless external suppliers. The obtained catalyst is thought to become more efficient in order to be able to avoid the post curing process. A complete characterization of silicone formulations processed will show the differences and similarities between the commercial and the new catalyst.

However, despite the remarkable advantages obtained by using the own technology catalyst, the work done until this point will show that the post-curing stage is still required in order to fulfill certain regulatory requirements. **Chapter 3** is focused on thoroughly characterizing all the phenomena occurring during the post-curing process. The results obtained will prove that, for the elastomeric formulation studied in the present work, post-curing cannot be avoided by optimizing the curing system but by means of influencing in other features of the production line.

Finally, **Chapter 4** will present the optimization of the catalyst developed in Chapter 2 in order to improve significantly its stability and efficiency. The resulting network will be comparatively studied to reveal subtle changes that might render important benefits for the company regarding both, the properties of the final products and its economic profitability.

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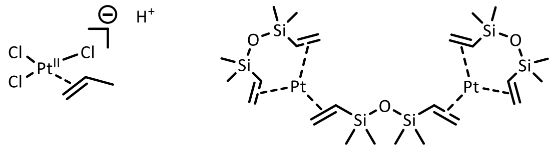
Chapter 2: Plant scalable Karstedt-like Pt-catalyst.

2.1. Introduction.

As it has been shown in the previous chapter, the platinum catalysed hydrosilylation reaction is a one of the most common procedures of curing sanitary silicone tubing applications.

Despite the fact that last scientific attempts have been focused on the search for low-cost transition metal [1–4] or even none metal-based catalyst [5], both Pt(II) and Pt(0) complexes are still the preferred to be used as hydrosilylation catalysts in the silicone rubber industry. This is because none of the non-platinum-based alternatives reported to date achieves the required TOF (i.e., catalyst's instantaneous efficiency)/TON (i.e., catalyst's lifetime robustness up to decay of activity) ratio for a high rate and low-cost silicone rubber production.

Among Pt complexes currently used (Figure 2.1), the Pt(0) one developed by Karstedt in 1973 [6] does still represent the benchmark for the rest. Unlike the initially used Speier's Pt(II) complex [7,8], Karstedt's one does not requires a dangerous in situ reduction, with the result that is activated by simple exchange of one of the 1,3-divinyltetramethyldisiloxane ligands (dvtms) for a molecule of the unsaturated substrate; this modification makes the complex more soluble in vinyl-containing silicone polymers; and it does also show a higher activity than Speier catalyst in the hydrosilylation of olefins. [9–11]



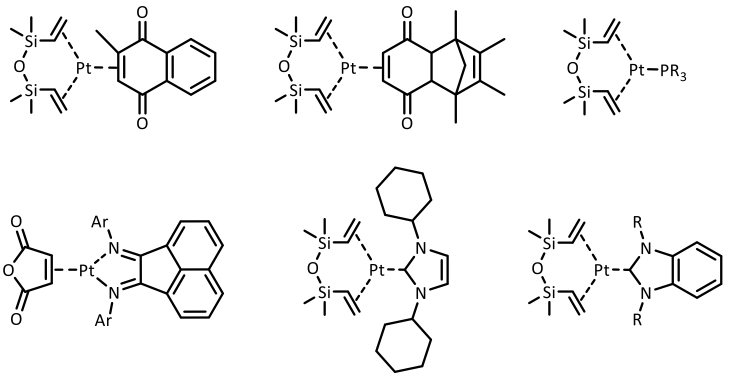
$H_2[PtCl_6]·6H_2O$/iPrOH
Speier's catalyst (1957)

Karstedt's catalyst (1973)

[Figure 2.1]: Most common Pt-based catalyst used in the silicone industry.

Despite its better characteristics, Karstedt's catalyst has still several aspects that can still be optimized. The most remarkable one is its tendency to decompose upon dissociation of both chelating and bridging dvtms on the view of the strong electron-donating β Si atom, forming platinum colloids. [12–14]

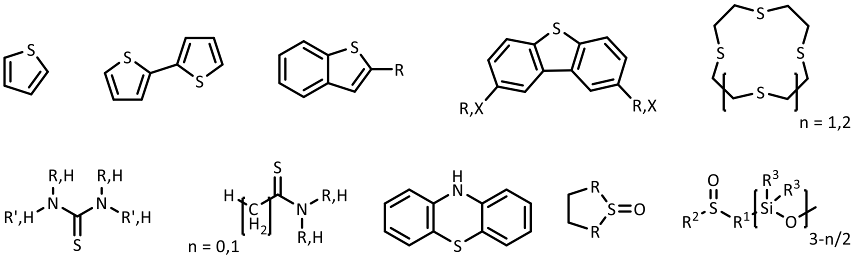
In the context of platinum-cured silicone rubber, these colloids could represent a serious concern regarding the quality of the obtained rubber product. Platinum colloids are reported to heterogeneously catalyze olefin's hydrogenation reaction. Such reaction could result in altering somewhat silicone rubber's curing. [15] Consequently, certain mechanical properties might also be affected since the cross-linking degree could be altered. Moreover, at high loads those metal colloids might eventually cause a haze in the reaction medium, leading to an unsightly yellowish taint to the rubber article. Therefore, research carried out on trying to increase the TON of Karstedt's catalyst avoiding colloid formation, is a topic of enormous importance to assure a low-cost platinum-cured silicone rubber production. In this sense, many attempts focus on strengthening the electron withdrawal ability of Karstedt's olefin ligand have been described on the literature (Figure 2.2). For instance, it has been reported that the exchange of μ-η^4-dvtms bridging ligand with selected electron-deficient olefin as ligands such as naphthoquinones [16], bidentate N-ligands [17], or more stronger **π**-acceptor ligands such as phosphines [18–20] or N-heterocyclic carbenes (NHC) [21–23], can protect against catalyst degradation and Pt colloid formation.



[Figure 2.2]: Some modified Karstedt's catalyst examples bearing electron withdrawing ligands already developed.

However, the ligands which form more stable Pt(0) complexes such as the ones of NHC and Ar-bian often results in a dramatically reduce of catalyst's TOF. Hence, the effective platinum load needed to achieve the same cross-linking degree is higher than when compared to the less stable Karstedt's catalyst that can overcome the above mentioned drawbacks. [9] Last but not least, in the field of platinum-cured sanitary silicone hose industry, using those stabilized Pt(0) complex instead of the Karstedt's one, will result into a significant increase in the overall hose-built cost, since the synthesis of these ancillary ligands requires multi-step sequences.[24,25]

Therefore, the aim proposed for this chapter is to develop an in-house made Karstedt's like catalyst. As prerequisites, the developed catalyst compound should show a reasonable TON; the synthetic procedure set should be economically viable, as well as easy to reproduce using the current resources of the company without implying a significant increase on silicone rubber processing's expenses. On this basis, a suggested solution is to take advantage of the great affinity of the Pt metal group towards other electron rich molecules such as those containing sulphur. However, in the field of platinum-cured silicone rubber applications, sulphur compounds are expected to strongly coordinate to Pt(0) centre, reducing consequently the catalyst's TOF. In fact, these compounds have been described to act as hydrosilylation inhibitors (Figure 2.3).



[Figure 2.3]: Some examples of hydrosilylation inhibitors based on thiophene; sulphoxides and organosilicon sulphoxides, phenothiazine, and macrocyclic thiocrown ethers. [26–29]

Even so certain, sulphur-containing compounds have proved to promote the hydrosilylation reaction under certain conditions. For instance, the addition of elemental sulphur [30] as hydrosilylation promotor has been reported, but the sulphur must be added in very well-defined amounts in order not to work as a hydrosilylation inhibitor. Recently, better results are reported to be obtained when adding ten times more Et_2S than platinum content. [31] More specifically, the addition of such excess of thioether to Karstedt's catalyst has not only effectively proved to prevent catalyst reductive deactivation, but it also results in higher reaction rate for the hydrosilylation of both tetravinylsilane, and vinyltrimethylsilane with chlorodimethylsilane. In addition, contrary to alkenylsulfides and homoallyllicthiothers, Et_2S is inert to hydrosilylation reaction so that, it does not compete with olefin substrate bonding. Finally, it is enough volatile to be easily heat-removed from the reaction mixture. All these features have made Et_2S an excellent ligand to stabilize noble metal catalyst such as the one of Karstedt.[31] Unfortunately, Et_2S has an extremely low flash point (-10 °C) therefore their use on large scale is unlikely for workplace security reasons. As a first approach, in the present work it has been chosen to study the effect of adding a less inflammable thioether such as Pr_2S with regards to the TON and TOF of Karstedt's catalyst. In this sense, the main challenges to face on this chapter are:

- Developed a synthetic methodology which enables the company to produce their own Karstedt's like catalyst at the lowest platinum cost possible.
- Study the effect of adding Pr_2S to Karstedt's catalyst as a way to stabilize it from reductive deactivation, both at short and long-term. So that, any uncertainty occurred

during storage conditions, or transportation e.g., will not badly effect on catalyst's shelf-life.

- Study the curing performance of the developed catalyst by means of comparing both curing behaviour and silicone rubber's mechanical profile in a real food grade silicone rubber compound, against the ones obtained when using the commercial catalyst. These studies would determine if the developed catalyst compound could be considered as a real alternative candidate which could be used for manufacturing platinum-cured silicone hose sanitary applications.

2.2. Materials and methods.

2.2.1. Reagents and materials.

Argon 5.0, purchased from Carburos Metalicos, was directly used without previous further drying. Dipropyl sulfide 97 % and Hexachloroplatinic (IV) acid hydrate 99.9 % trace metal basis (lot: MKB5063V), was purchased from Sigma Aldrich. Anhydrous 2-propanol (i-PrOH) 99.8 % and 1,3-divyniltetramethyldisiloxane 97 %, were purchased from Acros Organics. Polydimethylsiloxane fluid with a viscosity of 20 cSt, (Bluesil® FLD 47 V 20) and dimethylsiloxane, methyl vinyl gum, (Bluesil® 753) were supplied from Elkem Silicones. Hydrochlorhydric acid 37 %, nitric acid 65 %, perchloric acid 70 % as well as hydrofluoric acid 40 % were all of trace metal grade.

All of them were used as received except, for 1,3-divyniltetramethyldisiloxane, that was first dried over 3 Å molecular sieves, which were previously heated overnight at 120 ºC and vacuumed dried afterwards. Specially care was also taken for hexachloroplatinic (IV) acid hydrate during its manipulation, due to its hight hygroscopicity. More specifically, weighing and handling of this reactive were carried out under Ar atmosphere.

Commercially available platinum-cured silicone rubber was supplied from Shin-Etsu Chemical as a three-part system KE-561U/C-25 A/B. In which KE-561U is a FDA (21 C.F.R. 177,2600) and BfR compliant vinyl-containing polydimethylsiloxane HCR base; C-25 B (Lot: 1161800156 valid from 25-05-18 to 25-05-20) contains the hydrogenmethyl- dimethylsiloxane cross-linking polymer plus a catalyst inhibitor; and C-25 A (Lot: 1161800155 valid from 25-05-18 to 25-05-20) contains a stabilized platinum catalyst in the form of a vinyl-containing silicone gum paste. The utilized mixing for the HCR base plus the two-part addition curing agents A and B, was of 100:0.5:2 parts per hundred rubber (phr), respectively. Cross-linking was carried out by heating the blend at 120 ºC for 10 minutes under a pressure of approximately 40 MPa. Finally, the obtained silicone rubber sheet was post-cured in a hot air circulating oven for 4 hours at 200 ºC and allowed to temperate at room temperature for at least one full day prior perform any measurement.

2.2.2. BAS Pt catalyst's synthesis and compounding.

Hexachloroplatinic (IV) acid hydrate (0.50 g, 1.22 mmol) was accurately weight and kept into a sealed 25 ml round-bottomed flask under an Ar stream. Then, it was quickly transferred to a 250 ml three-necked Schlenk flask equipped with a reflux condenser and a funnel charged with $NaHCO_3$ (0.820 g, 9.76 mmol) under Ar stream. Thereafter, it was dissolved with 10 ml of anhydrous i-PrOH using a syringe purged with Ar. The orange mixture was stirred and heated to 70 ºC for 30 min under Ar stream, while it was being protected from light and then cooled down to room temperature. Solid $NaHCO_3$ was added portion wise over 5 min. The evolved CO_2 was vacuumed evacuated from the reaction Schlenk flask. The flask was then filled again with argon. After 10 minutes, degassed dry 1,3-divynil-1,1,3,3-tetramethyldisiloxane (2.2 ml, 9.72 mmol) was added via cannula and the reaction vessel was heated to 70 ºC for another 60 min. After confirming the completion of the reaction by TLC, the final off white suspension was cooled down to room temperature. Then the crude was vacuum filtered through a plug of silica gel/Celite®R566/$MgSO_4$ (v./v./v. 1:1:1) under Ar stream and wash out with additional 10 ml of anhydrous i-PrOH. The obtained pale-yellow filtrate was collected in a 50 ml Schlenk round-bottomed flask, which had been previously charged with 5 ml of Bluesil® FLD 47 V 20. Finally, solvent excess was vacuum distilled under inert atmosphere while its was cooled with a solid CO_2-acetone bath, up to yield a pale-yellow PDMS oil solution of $[Pt_2(dvtms)_3]$ complex. This one was stabilized by adding Pr_2S (2.8 ml, 19.25 mmol) with an Ar purged syringe. Storage at 8 ºC under Ar atmosphere for several months showed no degradation.

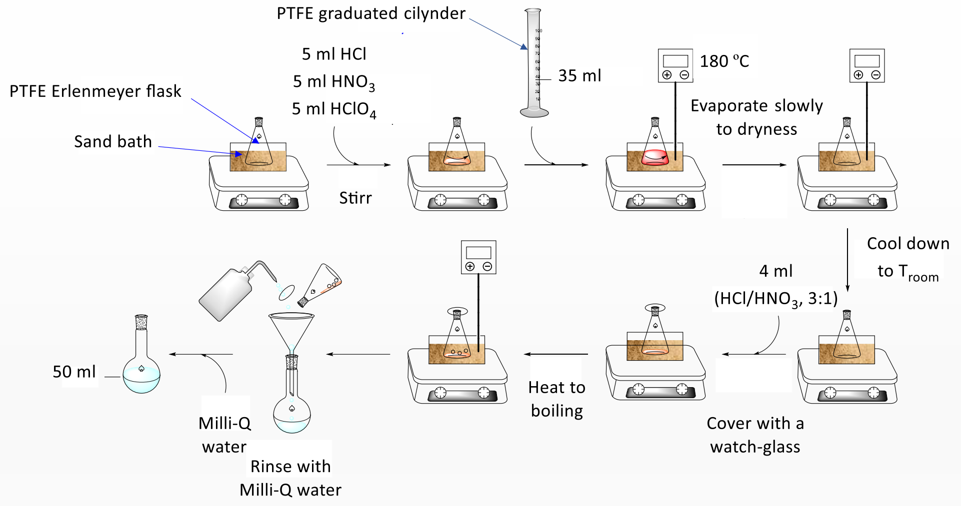
The follow up the reaction was carried out by thin layer chromatography on Merck Millipore F254 silica gel plates (200 µm thickness, polyester supported) drawn up in dichloromethane-cyclohexane mixture (v./v. 1:2). The spots were visualized by projecting ultra-violet light (254 nm) onto the sheet.

The obtained PDMS oil solution of BAS Pt catalyst was dropwise compounded with BlueSil™ 753 VMQ on an opened two-roll rubber mixing mill (2RMM), so that the Pt atom content in the silicone gum compound was approximately of 0.1 w./w. %.

2.2.3. Quantitative determination of Pt using ICP-AES.

Platinum content determination from both commercial and in-house made Karstedt's catalyst (BAS) was carried out with a Perkin Elmer Optima 2100V inductively coupled plasma atomic emission spectrometer (ICP-AES), using an internal standard. Quantitative recovery of platinum metal was achieved by subjecting the Pt catalyst to acid digestion procedure as stated for preparing the test solution used for quality control of talc described at the European Pharmacopeia. [32] The choice of this methodology was done in order to ensure the complete digestion of silicone polymer matrix. In this sense, HF acid constitutes the only appropriate acid to digest silicone polymer.

Sample's acid digestion was performed in the fume hood using a 250 ml PTFE Erlenmeyer flask (Figure 2.4).



[Figure 2.4]: Silicone's acid digestion procedure for quantitative recovering of Pt.

Approximately to 0.050 g of sample in the gum form or alternatively 10 µl of catalyst sample in the PDMS oil form, 5 ml of HNO_3 acid, 5 ml of HCl acid and 5 ml of $HClO_4$ were added. Then, 35 ml of HF was carefully added using a PTFE graduated cilynder to the previous dispersion and gently stirred up to the silicone compound sample was complete dissolved into H_2SiF_6. [33] Then, the obtained acid solution was evaporated slowly to dryness on a sand bath heated to 180 °C and cooled to room temperature. Then, the residue was reconstituted with 4 ml of aqua regia (HCl/HNO_3, 3:1), covered with a watch-glass, and heat to boiling. While it was still hot the aqua regia solution was transferred to 50 ml sized volumetric flask which was broad to volume with Milli-Q water, yielding an aqueous solution with approximately an 8 % of aqua regia. Quantitative recovering of Pt was ensured by rinsing with Milli-Q water the Erlenmeyer flask as well as the watch-glass.

2.2.4. Short and long-term stability studies.

Platinum colloids' formation was evaluated by means of visually colour matching with Pt/Co APHA-HAZEN coloured glass standards both at short and at long term. More specifically, a first assay was conducted to evaluate the deactivation of the catalyst during its usage for two months, whereas a second one was conducted to evaluate its long-term stability after a year of storage, during the two following months.

2.2.5. Silicone rubber's cure kinetics analysis.

Dynamic differential scanning calorimetry analysis in a Metter Toledo DSC822e, was used to study the catalytic activity of the developed catalyst against the one shown by the commercial one in cross-linking of VMQ silicone base KE-561U with the hydride cross-linking agent C-25B. Uncured samples were heated from 30 to 300 °C at various heating rates (2, 5 and 10 °C·min^{-1}) in nitrogen gas with a flow rate of about 50 ml·min^{-1}.

The activation energy of the reaction was then calculated using the Kissinger method. More specifically, the basic equation of this method is derived from the general rate equation of single step process (Eq. 1) which is expressed as a function of two variables, temperature (T) and the reaction model, f(α).

$$\frac{\partial\alpha}{\partial t} = k(T) \cdot f(\alpha) \quad \text{[Eq.2.1]}^{34}$$

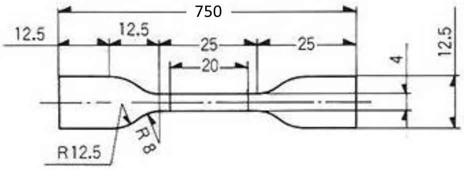
The temperature dependence of the process rate is typically parameterized through the Arrhenius equation: $k(T) = k_0 \cdot e^{-E_a/R \cdot T}$. Where k_0 and E_a are the preexponential factor and the activation energy respectively, and R is the universal gas constant (8.3145 J·mol^{-1}·K^{-1}). [35] Under linear heating rate condition, is assumed that the reaction rate reaches the maximum at the temperature (T_p) where DSC curve displays the peak. So that at this point, $\frac{\partial^2\alpha}{\partial t^2} = 0$ and from Eq.1 is obtained the Kissinger equation (Eq.2):

$$\ln\left(\frac{\beta}{{T_p}^2}\right) = \ln\left(-\frac{k_0 \cdot R}{E_a} \cdot \frac{\partial f(\alpha)}{\partial\alpha}\right) - \frac{E_a}{R \cdot T_p} \text{[Eq.2.2]}^{35}$$

For a set of DSC curves with different heating rates (β), $\ln\left(\frac{\beta}{{T_p}^2}\right)$ quantity plotted against the one of $1/T_p$, should give rise to a straight line whose slope turns the activation energy. [36]

2.2.6. Characterization of silicone rubber’s mechanical properties.

Finally, BAS Pt catalyst’s performance was further assessed by means of comparing post-cured rubber’s mechanical properties of the obtained silicone elastomer against the ones shown when using the commercial one. Statistical analysis was performed using IBM® SPSS® Statistics (ver 23.0, IBM® Co., USA). Rubbers mechanical properties’ measurements were all performed on 2 mm thick dumb-bell shaped specimens (type: SDMK 1000) according to ISO 37-2 (Figure 2.5).



[Figure 2.5]: SDMK 1000 dimensions according to JIS K6251-6, ISO 37-2, DIN 53504-S2, etc. All the values are expressed in mm.

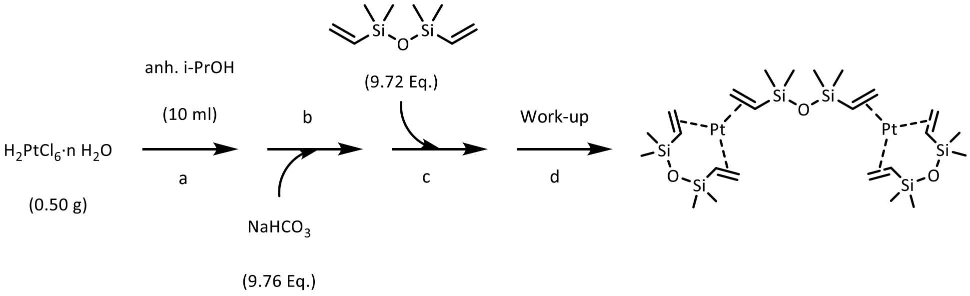
More specifically, ten SDMK 1000 specimens were used to determine silicone elastomer’s density, hardness, tensile strength, and elongation at break. Prior to analysis, the specimens were rinsed twice with Milli-Q water, dried, individually labelled and stored in sealed polyethylene bags.

Density was measured using the test method A described in ASTM D792–13 standard. A Micro IRHD digital electronic durometer (Hildebrand-GmbH) was used to perform micro–International Hardness Degree (IRHD) measurements according to ISO 48. Finally, both tensile strength and elongation at break were measured on 5 kN Zwick/Roell Z005 universal testing machine at room temperature in displacement control at a traction rate of 500 mm·min^{-1}.

2.3. Results and discussion.

2.3.1. Synthesis of Karstedt's catalyst.

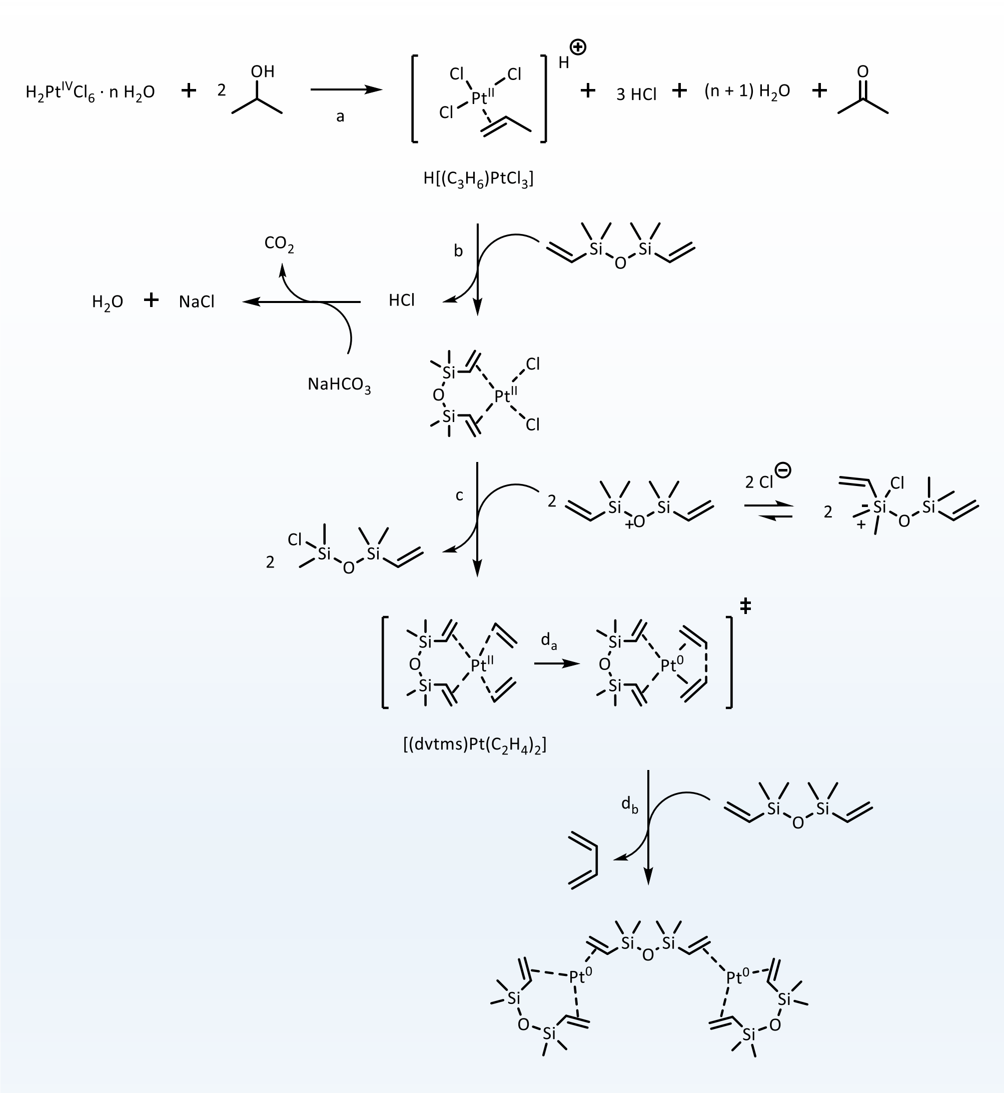
[$Pt_2(dvtms)_3$] complex in 5 ml polydimethylsiloxane oil form was synthetized based on the one-pot methodology reported by Dierick and Markó [37] (Figure 2.6).



[Figure 2.6]: Synthetic scheme for preparing [$Pt_2(dvtms)_3$] complex. Reaction conditions: a) 30 min at 70 °C, b) Portion wise addition over 5 min at T_{room}, and c) 1 h at 70 °C. Work-up procedure: d) Filtration (Celite®R566, SiO_2 gel, and $MgSO_4$: 1/1/1 in volume) and elution with i-PrOH (2x10 ml), e) Collect the filtrate in 5 ml of PDMS oil (Bluesil ® FLD 47 V 20), and f) Solvent excess vacuum distillation until reaches a final volume of 5 ml.

The use of polydimethylsiloxane oil was though in order to make the catalyst compounding with silicone easier.

More specifically, Karstedt's catalyst was prepared on 0.5 g scale in two step reduction process from Pt(IV) in H_2PtCl_6 to Pt(0) by dvtms. The mechanism for this reduction process is illustrated in Figure 2.7:



[Figure 2.7]: Mechanism for the main reduction pathway of H_2PtCl_6 into $[Pt_2(dvtms)_3]$: a) H_2PtCl_6 reduction into $H[(C_3H_6)PtCl_3]$ by i-PrOH, b) Cl/C_3H_6 ligand substitution with dvtms, c) Chloride-mediated double transmetalation of Pt-Cl bonds with dvtms via the electrophilic attack of $[(dvtms)PtCl_2]$ on the ipso carbon of the activated pentavalent vinylsilane, and d) 1,3-butadiene reductive elimination from transient $[(dvtms)Pt(C_2H_4)_2]$ intermediate concomitant with ligand substitution with dvtms. [38]

Giving the fact that H_2PtCl_6 is highly hygroscopic, the weighing and handling of this reagent was carried using a dry, Ar filled MBRAUN UNIlab glovebox. Both anhydrous i-PrOH and dvtms were roughly degassed by repeated sonication under light vacuum for 5x1 min and refilling the atmosphere with Ar. All transfer operations were conduct by using an air free stainless-steel cannula (16-gauge x 24 in length).

According to the experimental conditions described by Dierick and Markó, [Pt_2(dvtms)$_3$]'s synthesis was first carried out using a Schlenk line. This is because, in the oil form this complex has been reported to be somewhat thermally, photochemically and aerobically sensitive as well, tending to deposit platinum metal. [39] In addition, special care was also taken while performing its synthesis by covering the reaction vessel with an aluminium foil, since the rate of Pt^{IV}/Pt^{II} redox reaction (Figure 2.7, a) has been also reported to be negatively affect by light.[31] Nonetheless, preparing Karstedt's catalyst under such strict air and moisture free conditions can only be accomplished on a preparative laboratory scale at most, due to the cost of equipment as well as time consumed in both reagents and equipment's conditioning, as well as in liquid convey operations. Indeed, at industrial scale, only purging technique is currently possible for effective achieving the atmospheric inerting required for the synthesis of air- and moisture-sensitive compounds. Although this will require massive quantities of N_2 gas since the use of Ar gas is probably unfeasible due to its cost. Therefore, from the industrial point of view, it would be interesting to modify the [Pt_2(dvtms)$_3$] complex's current synthetic conditions so that, the synthetic procedure can be easily scaled up and carried out without needing to use such complex Schlenk techniques.

On this basis, a second batch of [Pt_2(dvtms)$_3$] complex in polydimethylsiloxane oil form was synthetized starting from 1.00 g of H_2PtCl_6. However, in this case the handling of this reagent was performed using a round bottomed flask under Ar stream, which was immediately sealed afterwards with a septum for weighting. Solvent as well as dvtms were added to the reaction vessel using a syringe which was previously purged with Ar. The reduction process of H_2PtCl_6 into [Pt_2(dvtms)$_{3]}$ was also conducted under Ar atmosphere. After confirming the completion of the reaction, the crude was poured, and vacuum filtered through a plug of silica gel/Celite®R566/$MgSO_4$ (v/v/v 1:1:1) under Ar stream. The filter cake was wash out by adding 10 ml of anhydrous i-PrOH. The pale-yellow filtrate was collected in a 50 ml Schlenk round-bottomed flask, which was previously charged with 5 ml of Bluesil® FLD 47 V 20. Finally, solvent excess was vacuum distilled under inert atmosphere up to yield 5 ml of pale-yellow PDMS oil solution of Karstedt's catalyst with a Pt atom content of 45520 $mg \cdot l^{-1}$ as determined by ICP-AES (sample preparing is described in methods section).

Therefore, it has been proved that with a simple laboratory installation, Karstedt's catalyst could be easily prepared on regular basis without the need for large industrial installations.

However, to guarantee platinum-cured silicone rubber production's autonomy to the company, the limiting factor still is the platinum metal price. So that, thinking on the scaling-up catalyst's synthesis from laboratory to pilot plant scale, two bulk producers and suppliers of H_2PtCl_6 99.9 % were contacted to achieve a more competitive metal price.

2.3.2. Catalyst's bulk price.

The quotes for both 50 g and 1 kg were purchased at D.F Goldsmith Chemical & Metal Corp and Colonial Metals, Inc. H_2PtCl_6's unit price as well as the total cost including the shipping to Venair headquarters are summarized in table 2.1.

[Table 2.1]: $H_2PtCl_6 \cdot n\ H_2O$ quotes.

Qty (g)	Supplier			
	D.F. Goldsmith		*Colonial Metals*	
	Price Unit	Total	Unit price [a]	Total
50	45.40	2675	31.00	1550
1000	14.90	15588	12.57	12570

[a] The shipping cost to Venair headquarter was included in product's unit price.

As it can be seen in the above table the quotes for H_2PtCl_6 offered by Colonial's are more affordable than the ones purchased on D. F. Goldsmith. When compared these quotes with regards the one of commercial Pt catalyst, Colonial's quote for 1kg of this reagent would allow for ensuring two years of platinum-cured silicone hose processing at Venair Ibérica production plant.

Moreover, if compounded with a silicone gum so that the Pt content was the same as in Shin-Etsu C-25 A Pt catalyst (929.4 $mg \cdot Kg^{-1}$ as determined by ICP-AES), the in-house made Karstedt's catalyst would have almost same price per kg of silicone gum compound (Table 2.2):

[Table 2.2]: Comparison between catalysts.

Catalyst	Pt (g)	Gum compound (Kg)	€/Unit	HCR's production (years)
Shin-Etsu C-25 A	83.65	90	59.00	1
Karstedt	227.6 [a]	244.9	51.00 [b]	2.7

[a] Calculated from expected Karstedt catalyst PDMS solution's Pt amount (in grams) that would result after reacting 1000 g of H_2PtCl_6 (MW: 429.81 $g \cdot mol^{-1}$) having a Pt atom content of approximately 47.8 %.

[b] Unit priced was estimated with reference to Colonial Metal's quote.

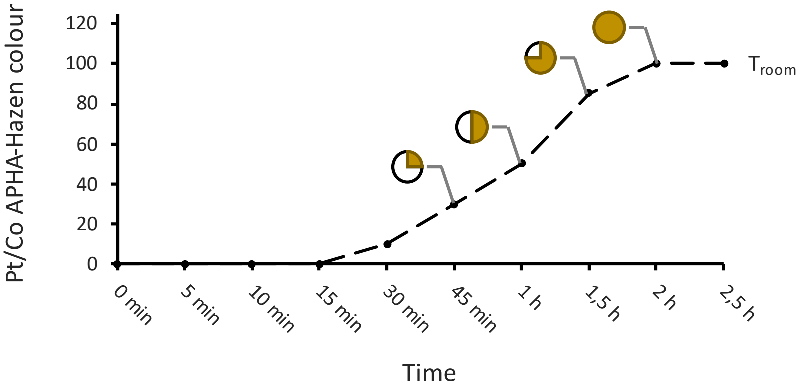
In terms of price the synthetized Karstedt's catalyst might not be seem at first competitive since it does not differ from the one of commercially supplied.

However, having this methodology for preparing their own catalyst provides a valuable know-how for the company, which would make it possible to gain competitive advantage over the rest sanitary platinum-cured silicone hose's producers since Venair's production lines would not need to depend on external suppliers.

2.3.3. Stability of Karstedt's catalyst in silicone oil solution.

Storage at -15 °C under Ar atmosphere, the obtained Karstedt's catalyst PDMS solution showed no degradation into platinum metal colloids for several days.

However, when exposed to normal conditions, the solution began to darken to brown colour after 15 minutes as illustrates the recorded APHA-HAZEN colour graph (Figure 2.8):



[Figure 2.8]: Karstedt catalyst's reductive deactivation rate at 25 °C. Filled circles represent the yellowness grade achieved (from left to right: 25 %, 50 %, 75 %, and 100 %). Room temperature stability study was conducted with 12.5 mg·l^{-1} Pt test sample in PDMS oil (40 ml) which was prepared using a reusable glove bag filled with Ar.

The graph also denotes that Karstedt's catalyst without adding a thioether stabilizer is as expected, very susceptible to reductive deactivation and it does not exceed one hour of pot-life.

2.3.4. Study of Pr_2S effect on Karstedt's catalyst reductive deactivation rate.

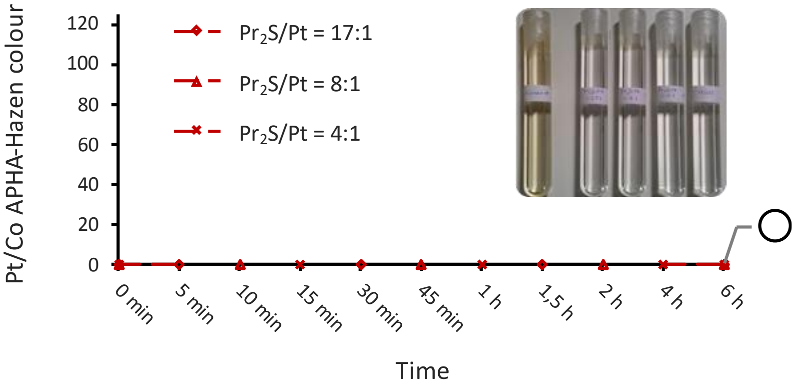
In order to study the suitability of Pr_2S as effective stabilizer of $[Pt_2(dvtms)_3]$ complex, Pr_2S/Pt's ratios of 17, 8 and 4 were prepared using a reusable glove bag filled with Ar.

More specifically, the following volumes of Pr_2S were accurately measured and added to 1000 µl aliquot of Karstedt's catalyst PDMS solution:

[Table 2.3]: Pr_2S/Pt mixtures prepared.

Karstedt catalyst aliquot (µl)	Pr_2S (µl)	Pr_2S/Pt ratio
1000	560	17:1
	280	8:1
	140	4:1

Then, sample tests were prepared by accurately measuring 11 µl from each of the Pr_2S/Pt mixtures, broad to 40 ml with PDMS oil into a volumetric Nessler tube and then the APHA-HAZEN colour changes were recorded up to 6 hours of exposition to normal conditions (Figure 2.9):



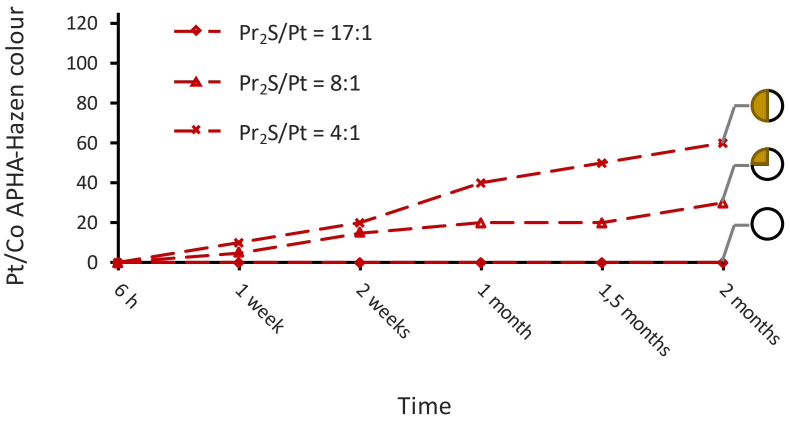
[Figure 2.9]: Pr_2S effect on $[Pt_2(dvtms)_3]$ complex reductive deactivation. The unfilled circle denotes that not darkeness on sample test solution was observed over the tested time.

As it can be seen, the recorded graphs denote that when Pr_2S was added to Karstedt's Bluesil® FLD 47 V 20, it does effectively prevent the reductive deactivation of $[Pt_2(dvtms)_3]$ complex. Therefore, its stability is improved.

2.3.4.1. Pr_2S/Pt short-term stability study.

A first assay was conducted to evaluate the deactivation rate of $[Pt_2(dvtms)_3]$ complex up to two months of exposition to normal conditions. The aim of this study was to assess whether the addition of Pr_2S to Karstedt's catalyst could lead to a compound with sufficient pot-life, so that it could be used in Venair Ibérica at regular basis as well as send to other production plants if required.

Recorded APHA-HAZEN colour changes are shown in the following Figure 2.10:



[Figure 2.10]: Short-term stability study of Pr_2S/Pt solutions.

As it can be seen, the above graph denotes that the highest is the amount of Pr_2S added to Karstedt's Bluesil® FLD 47 V 20 oil solution, the less susceptible it is to reductive deactivate. For instance, with a Pr_2S/Pt ratio of 17, $[Pt_2(dvtms)_3]$ complex's silicone oil solution remains clear and colourless even after 2 months of exposition to air and room temperature. Whereas with Pr_2S/Pt ratio of 8, platinum metal colloids were detected to begin form up to 2 months of exposition; and the one with a Pr_2S/Pt ratio of 4 does not exceed one month and half of pot-life.

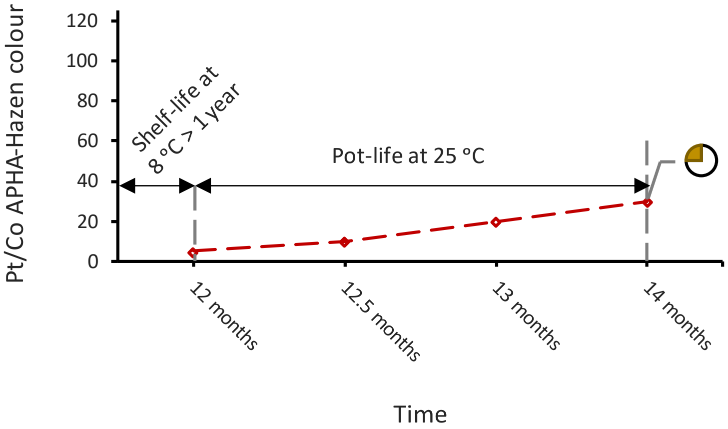
2.3.4.2. Pr_2S/Pt long-term stability study.

Base on the results obtained in short-term stability study, the stability of $Pr_2S/Pt = 17:1$ mixture was further evaluated after a year of storage at 8 °C during the two following months of exposition to normal conditions. The aim of this later study was to evaluate whether the in-house made Karstedt's catalyst with a Pr_2S/Pt ratio of 17 could be prepared and then stored for a prolonged time, without a significant increase in Pt colloids' formation.

Prior to conduct such test and because one of the principal goals in the present work is to provide a Pt catalyst compound with same characteristics as the commercially supplied to Venair, 30 µl aliquot of $Pr_2S/Pt = 17:1$ mixture prepared from concentrated Karstedt's catalyst PDMS solution was dropwise added to 109.2 g of Bluesil® 753 VMQ silicone gum and compound on the 2 RMM. So that the resulted BAS silicone paste has approximately a concentration in Pt of 12.5 $mg \cdot kg^{-1}$ as the rest of tests.

Finally, around 0.05 g of BAS silicone paste was weighted and placed into a modified Nessler tube, in which a shorter tube was introduced inside it. So that, APHA-HAZEN colour changes from such a more consistency Pt catalyst silicone dispersion could be measured without light reflecting problems.

Long-term stability results are illustrated in the following graph (Figure 2.11):



[Figure 2.11]: Long-term stability study for BAS silicone paste. Only after 2 months the compound was observed to begin to darken in colour.

As it can be seen, the recorded APHA-HAZEN colour graph shows that the developed BAS silicone paste can last as long as an unopened lot of Shin-Etsu's C-25 A under regular storage conditions. The commercial catalyst is reported to have a shelf-life of 1 year.

2.3.5. **Reactivity of Pr_2S/Pt catalytic system in comparison to the commercial Pt-catalyst for silicone polymer cross-linking reaction.**

2.3.5.1. Determination of the minimum effective Pt load.

The following silicone rubber compounds (1 to 8) were prepared by adding different amounts of BAS PDMS solution 45520 mg·l^{-1} in Pt. Commercial compound (control) was also prepared as reference. More specifically, these were prepared by blending first 100.0 g of KE-561U silicone base with 2 phr of Shin-Etsu's crosslinker C-25 B on the 2RMM. After 10 min of mixing, BAS or alternatively 0.5 phr of Shint-Etsu's catalyst C-25 A was added to the previous blend and mixed for another 5 min. The resultant silicone rubber compounds were cured by compression molding at a pressure of 40 MPa in a 2 mm thick mould at 120 °C for 10 minutes. Silicone rubber's curing was assessed by checking visually the elastomer's consistency. So that, the blends which got attached to the stainless steel mold or remain sticky after being demolded were discard.

[Table 2.4]: KE-561U / C-25 B compounds assayed.

Sample	KE-561U (g)	C-25 B (phr)	Catalyst		[Pt] (ppm) [a]	¿Was curing achieved?
			BAS	C-25 A		
1	100	2	65 µl	-	29.6	✓
2	100	2	52 µl	-	23.7	✓
3	100	2	39 µl	-	17.8	✓
4	100	2	16 µl	-	7.3	✓
5	100	2	13 µl	-	5.9	✓
6	100	2	12 µl	-	5.5	✓
7	100	2	11 µl	-	5.0	✓
8	100	2	10 µl	-	4.6	✗
Control	100	2	-	0.5 g	4.6	✓

[a] Calculated with reference to the amount of KE-561 U silicone base.

As it can be seen in table 2.4, the addition of 17-fold excess of Pr_2S to Karstedt's catalyst does not inhibit silicone rubber curing, since the obtained silicone rubber sheet was perfectly smooth and there was no detectable stickiness area on its surface. Moreover, the obtained silicone elastomer product is completely inodorous. This result suggests that despite having a higher boiling point than the one of Et_2S, Pr_2S is still enough volatile to be completely remove after cross-linking reaction.

Regarding the minimum effective Pt load, this was found to be 5.0 ppm (compound 7). This amount is almost the same as the one quantified in Shin-Etsu's silicone gum paste C-25 A by ICP-AES. Hence, the use of the developed BAS Pt catalyst instead of the commercial one would not result to an increase into overall platinum-cured silicone hose processing's cost, in terms of platinum's load.

Having demonstrated its potential as a stable and affordable hydrosilylation catalyst, the next step is to compare its performance in the silicone paste form against the one shown by the commercial catalyst. None of the previous achievements would have any industrial interest if the catalytic rate as well as the obtained silicone rubber mechanical response profile is not at least the same as the ones obtained with the commercial one.

2.3.5.2. DSC cure characterization.

With the aim of studying silicone's curing kinetic parameters, the following KE-561U compounds were prepared (table 2.5):

[Table 2.5]: Composition of the silicone rubber compounds.

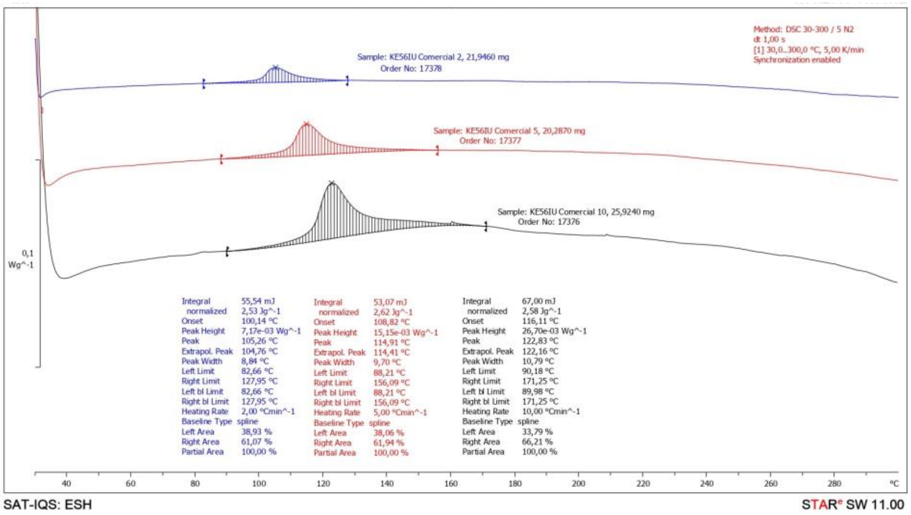
Sample	KE-561U (g)	C-25 B (g)	Catalyst (g)		[Pt] ($mg\cdot kg^{-1}$) [b]
			C-25 A	BAS [a]	
Control	100.1	2.003	0.508	-	4.7
BAS	100.1	2.003	-	0.507	5.1

[a] BAS Pt catalyst was prepared by compounding 5 ml of fresh prepared Pr_2S/Pt = 17:1 PDMS solution 45520 $mg\cdot l^{-1}$ in Pt with 227.3 g of Bluesil® 753 silicone gum on the 2RMM, so that 1 Kg of the resulted silicone paste has a Pt load of approximately 1001.3 $mg\cdot Kg^{-1}$.

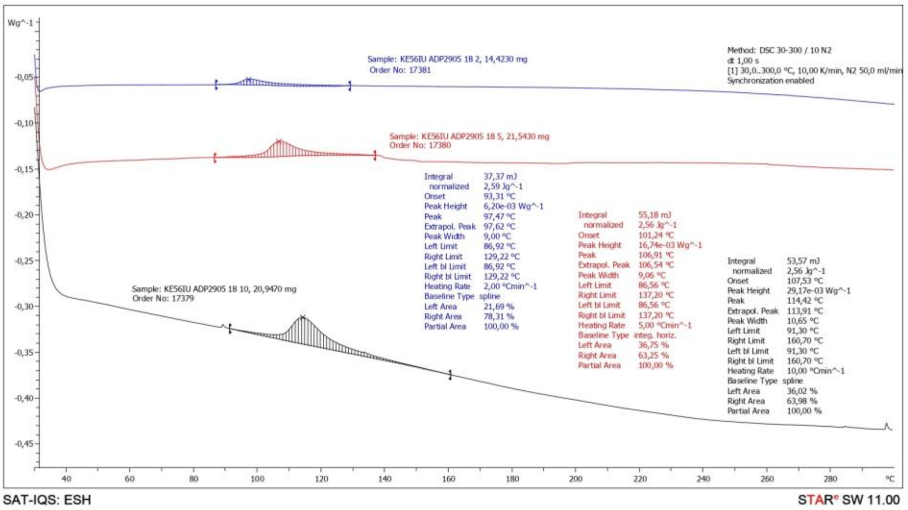
[b] Calculated with reference to the amount of KE-561 U silicone base.

Thereafter, their dynamic DSC curves were examined. More specifically, three different heating rates (β) were tested, and the results obtained are shown below:

Control



BAS



[Figure 2.12]: DSC curing curves for control (at the top) and BAS (down) addition curable silicone systems at heating rates of 2 °C·min^{-1} (blue), 5 °C·min^{-1} (red) and 10 °C·min^{-1} (black).

[Table 2.6]: Effect of heating rate on curing temperature and heat of reaction.

Sample	β (°C·min^{-1})	T_p (°C)	Heat of reaction (J·g^{-1})	
			ΔH_R	M ± SD
Control	2	105.26	2.531	2.577 ± 0.04
	5	114.91	2.616	
	10	122.83	2.585	
BAS	2	97.47	2.591	2.570 ± 0.02

Sample	β (°C·min^{-1})	T_p (°C)	Heat of reaction (J·g^{-1})	
			ΔH_R	M ± SD
	5	106.91	2.561	
	10	114.42	2.557	

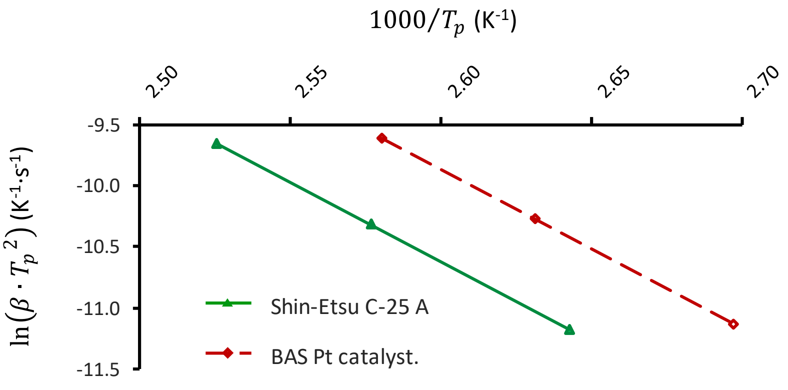
Where M refers to the average value for ΔHR and SD to its standard deviation.

As it can be observed, for all the heating rates tested, platinum-mediated vinyl-functionalized silicone's hydrosilylation is characterised by a single exothermal process, as shown in Figure 2.12. Moreover, the heat of reaction values obtained suggest that addition-curable silicone systems tested reach complete cross-linking regardless of the heating rate. Furthermore, when compared the two addition-curable systems assayed, the difference between average heat of reaction (table 2.6, M ± SD's column) was found to be negligible. This result suggests that the curing's mechanism of silicone elastomer when used the developed BAS Pt catalyst, does not differ significantly from the one shown with Venair's Pt catalyst of reference.

Aside from this information, DSC experimental data also allows for determining valuable kinetic parameters for the subsequent comparison of both hydrosilylation catalysts regarding their performance, such as the activation energy (E_a).

On this regard, Kissinger method was chosen due to its simplicity and accuracy in kinetic parametrization of single-step solid-state reactions under linear heating rate conditions. [40]

More specifically, the activation energy was obtained from the slope of $\ln\left(\beta/{T_p}^2\right)$ vs $1/T_p$ as shown in Figure 2.13 and summarized in table 2.7:



[Figure 2.13]: Kissinger plot for the cure of control and BAS silicone rubbers compounds.

[Table 2.7]: Results of the linear fitting shown in Figure 2.13.

Sample	E_a (KJ·mol-1)	r^2
Control	107.8	1.000
BAS	108.2	1.000

As it can be seen in the above table 2.7, the two addition-curable silicone systems have similar curing's energy barrier.

2.3.5.3. Mechanical properties.

In addition to the cure kinetic analysis, silicone's mechanical response characterization was also performed to assess the performance of BAS Pt catalyst compared with the commercial one over time. More specifically, two silicone rubber sheets were prepared using the same batch of the developed catalyst. The first was compounded with fresh prepared (F) BAS catalyst silicone paste and the second was compounded with the same after 6 months of storage (6M). Commercial silicone rubber sheets were also prepared on the same basis as reference. Composition of the samples tested are shown below (table 2.8):

[Table 2.8]: Composition of the silicone rubber samples tested.

Sample		KE-561 U	C-25 B (g)	Catalyst (g)	
				C-25 A	BAS
Control	F	100.1	2.017	0.507	-
	6M	100.0	2.006	0.502	-
BAS	F	100.1	2.014	-	0.505
	6M	100.0	2.001	-	0.501

Cross-linking was carried out by heating the blends at 120 °C for 10 minutes under a pressure of approximately 40 MPa. Finally, the obtained silicone rubber sheets were post-cured in a hot air circulating oven for 4 hours at 200 °C and allowed to temperate at room temperature for at least one full day prior perform any measurement.

Table 2.9 shows data recorded from each of them:

[Table 2.9]: Density ($\rho_{23^{\circ}C}$), IRHD, tensile strength (σ_{max}) and elongation at break (ε_{max}) measured from control and BAS silicone rubber samples at two levels of catalyst's storage time (F and 6M).

Variable	Sample	F	6M
$\rho_{23^{\circ}C}$ ($g\cdot cm^{-3}$)	Control	1.1588, 1.1593, 1.1564, 1.1600, 1.1567, 1.1582, 1.1585, 1.1571, 1.1580, 1.1570	1.1573, 1.1563, 1.1559, 1.1554, 1.1559, 1.1566, 1.1573, 1.1569, 1.1573, 1.1587
	BAS	1.1551, 1.1593, 1.1544, 1.1567, 1.1584, 1.1569, 1.1556, 1.1570, 1.1558, 1.1564	1.1573, 1.1578, 1.1575, 1.1572, 1.1568, 1.1572, 1.1578, 1.1570, 1.1571, 1.1582
IRHD	Control	64.9, 64.4, 66.0, 64.0, 65.3, 64.8, 64.9, 62.3, 65.1, 66.0	64.1, 64.3, 64.6, 65.4, 64.6 63.9, 63.9, 64.4, 64.8, 63.9
	BAS	65.6, 65.1, 65.5, 66.4, 67.0, 65.9, 65.6, 66.0, 64.4, 64.0	64.1, 63.6, 64.8, 64.8, 65.1, 63.1, 64.0, 65.8, 66.0, 67.0
σ_{max} (MPa)	Control	12.21, 10.80, 10.79, 11.96, 12.57, 11.78, 11.34, 11.86, 12.50, 10.69	10.96, 10.27, 10.28, 10.76, 9.79, 10.91, 10.15, 11.96, 10.86, 9.83
	BAS	12.17, 11.83, 11.39; 11.57, 12.21, 11.26, 11.24, 10.71, 11.05, 11.10	10.98, 11.89, 9.93, 10.45, 9.08, 10.32, 11.90, 10.91, 9.84, 10.36
ε_{max} (%)	Control	425, 366, 368, 356, 385, 340, 342, 363, 404, 324	437, 333, 376, 366, 374, 379, 349, 415, 378, 312
	BAS	408, 380, 356, 395, 395, 363, 393, 321, 417, 344	418, 487, 354, 374, 318, 411, 415, 402, 369, 370

A two-way ANOVA was performed to study whether the mechanical properties of KE-561U post-cured silicone rubber are affected by the catalyst used as well as the storage time of the same at a 1 % level of significance.

Descriptive statistics and ANOVA test results are summarised in the following table 2.10 and 2.11, respectively:

[Table 2.10]: Descriptive statistics.

M ± SD:	Control		BAS	
	F	6M	F	6M
$\rho_{23^{\circ}C}$ ($g\cdot cm^{-3}$)	1.1580 ± 0.0012	1.1568 ± 0.0010	1.1580 ± 0.0015	1.1574 ± 0.0004
IRHD	64.8 ± 1.1	64.4 ± 0.5	65.6 ± 0.9	64.8 ± 1.2
σ_{max} (MPa)	11.65 ± 0.71	10.58 ± 0.65	11.45 ± 0.49	10.57 ± 0.89
ε_{max} (%)	367 ± 31	372 ± 36	377 ± 30	392 ± 46

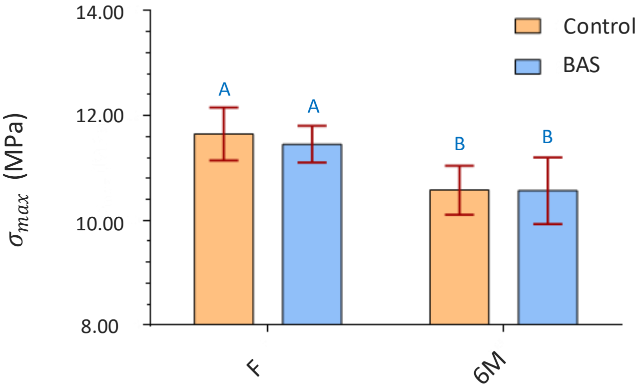
[Table 2.11]: Two-way ANOVA table.

Variable	Variability's source					
	Cat.		t_{stg}		*Cat.* x t_{stg}	
	F-test	p-value	F-test	p-value	F-test	p-value
$\rho_{23°C}$	4.0	0.052	2.3	0.13	2.3	0.14
IRHD	4.1	0.049	3.4	0.074	0.3	0.57
σ_{max}	0.2	0.64	19.7	< 0.001	0.2	0.68
ε_{max}	1.7	0.20	0.7	0.41	0.2	0.67

Where Cat. refers to the catalyst factor, t_{stg} to storage's time and Cat x t_{stg} to their interaction.

ANOVA test results denote the same average mechanical properties of the post-cured silicone material is obtained, regardless of the catalyst used for the curing.

In addition, Sidak's follow-up test to ANOVA revealed that although silicone rubber's ultimate tensile strength mean might be affected by catalyst's pot-life, the developed catalyst behaves on the very same manner as the commercial one as shown in Figure2.14:



[Figure 2.14]: Time-evolution of σ_{max} for both commercial and BAS-cured silicone rubbers. Error bars indicates the 99 % CI of the mean. Means sharing a letter are not significantly different according to Sidak's adjusted p-value.

2.4. Concluding remarks.

Chapter 2 shows the development of a plant-scalable in-house made catalyst for silicone elastomer's addition curing. On this regard, a one-step synthetic procedure has been proposed for preparing [Pt_2(dvtms)$_3$] complex just by using an Ar stream instead of the strict inert techniques traditionally used in organometallic chemistry. The results obtained, suggest that the synthetic procedure proposed could be easily reproduced at a kg-scale with a considerable small reaction's volume. Furthermore, with the same metal's cost per Kg of silicone paste compound as the one of external supplied Pt catalyst could be assured. Purchasing 1 kg of H_2PtCl_6 99.9 % would ensure Venair Ibérica production's plant for two entire years of platinum-cured silicone hose processing.

Stability studies showed that, it has been proved that the addition of an excess of Pr_2S to fresh prepared [Pt_2(dvtms)$_3$] complex does effectively prevent its reductive deactivation upon exposition to standard conditions. Bests results were obtained with a Pr_2S/Pt ratio of 17. The resulted Pt PDMS oil solution did not show evidence of Pt colloids formation over the first two months to exposition to air atmosphere and room temperature. Furthermore, once compounded with gum, long-term stability studies denoted that under the appropriate storage conditions, BAS silicone paste could be prepared on large scale and then stock for a reasonable prolonged time. Results showed that this Pt compound present the same shelf-life as the one of Shin-Etsu's commercial Pt catalyst.

When tested BAS's performance as hydrosilylation catalysts, the tests showed that, when the developed Pt-catalyst is used, silicone's cross-linking was achieved with the same curing conditions as with the commercial catalyst. Regarding the minimum Pt load for curing of silicone rubber, this was found to be 5.0 $mg \cdot kg^{-1}$ of KE-561 U silicone base. This result proves that is possible to use the in house made catalyst at the same ratio as specified for C-25 A commercial catalyst. Moreover, KE-561U/C-25 A's curing kinetic characteristics are not altered when used the developed catalysts.

Characterization of silicone rubber's mechanical properties denotes that there is no meaningful difference between using either BAS or Venair's commercial catalyst of reference.

In summary, the developed BAS's catalyst could be considered as a promising hydrosilylation catalyst to substitute the commercial one, making Venair gain more control over its production lines.

In the following chapter, the influence of the catalyst in the post-curing stage of production will be analysed in order to stablish the impact of the catalyst system. It is thought that improved efficiency of BAS catalyst might make unnecessary the post-curing enhancing the productivity.

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Chapter 3: Post-curing study.

3.1. Introduction.

As it has been shown on previous chapters, the favourable properties of platinum-cured silicone rubber are of great interest for many sanitary applications. Such properties are also preserved when used the developed BAS's catalyst instead of the one of Shin-Etsu's C-25 A commercial catalyst for VMQ silicone elastomer's addition curing.

Although this curing system is preferred over peroxides, most of pharmaceutical and food-grade silicone hose's producers still must use to post-cure the silicone rubber in order to ensure that their product complies with the strict low migration level of either unreacted oligomers, additives, catalysts, or breakdown products demand by such sensitive areas.

Particularly, in the context of food contact applications (FCM), the European Commission includes silicone materials on their list of FCM articles and materials for which specific measures shall be established (Framework regulation (EC) No. 1935/2004 [1]). However, at EU level there is still no consensus on to specific requirements to take for these materials. In absence of such harmonized regulation the Council of Europe (CoE) has propose a resolution Ap (2004) 5 [2], but it is not expected to be mandatory unless it is transposed into national laws soon. Instead, several country specific regulations exist, but a few key ones have emerged as major standards that are accepted by many countries. For instance, the German Bundensinstitut für Riskobewertung (BfR), section XV for silicone rubber [3] and the United States FDA 21 CFR177.2600 "Rubber articles for repeated use"[4] are both the most widely accepted standards by European countries. [5]

The present work will address the post-curing issue in the context of FDA 21 CFR177.2600. This is because it involves the main food contact regulations from which Venair's sanitary silicone hoses must comply to access food & beverage's market. More specifically, in this chapter it will discuss whether by optimizing the curing system could be possible to eliminate this additional cure step so that, it could be obtained a more cost competitive product.

On this sense, the following objectives will be covered:

- Study the effect of catalyst on silicone elastomer's thermogravimetric profile during post-curing.

- Determine the overall migration in aqueous and fat simulants from both not post-cured and post-cured KE-561U silicone elastomers when used BAS's catalyst for the curing.
- Qualitative analysis of the migration residue using Gas chromatography-mass spectrometry technique (GC-MS) in order to intelligently attempt to reduce their amount in the rubber compound.
- Rethink post-curing's process based on the results obtained and present alternatives.

3.2. Materials and methods.

3.2.1. Chemicals.

Dichlorodimethylsilane ($Si(CH_3)_2Cl_2$) ≥ 98.5 % (GC), was purchased from Sigma-Aldrich. n-hexane ≥ 95 5, HiPerSolv CHROMANORM® for HPLC was purchased from VWR Chemicals and used as received. Octamethylcyclotetrasiloxane (D_4) (99.8 %, Sigma-Aldrich, LOT: 10502PC) and decamethylcyclopentasiloxane (D_5) (98.1 %, Sigma-Aldrich, LOT: 03011DJ) were used as external standards.

3.2.2. Thermogravimetric analysis.

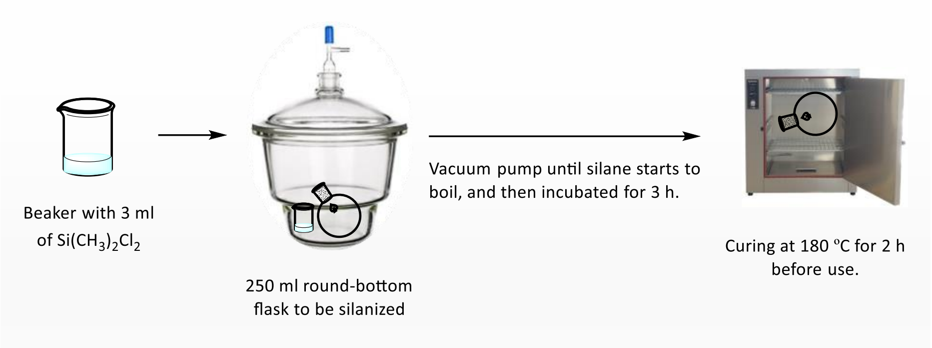
Platinum-cured silicone test specimens (approximately 20 mg) were cut and their weight loss during post-curing was recorded using a Mettler-Toledo TGA model TG30 operating under isothermal mode (200°C for 4 hours) and with an air gas flow of 50 $ml \cdot min^{-1}$.

3.2.3. Migration tests into food simulants.

In order to qualify the silicone rubber as a safe material for food & beverage's extrusion applications; reflux extraction tests were carried out as described in paragraph e and f of United States standard FDA 21 CFR177.2600 with the following specifications:

3.2.3.1. Migration into Milli-Q water.

Prior to perform aqueous migration test, active hydroxyl groups on glass surface were deactivated with $Si(CH_3)_2Cl$ (Figure 3.1). So that it would be minimised the loss of hydrophilic solute by adsorption onto the walls of the container.



[Figure 3.1]: Glasware silanization procedure· [6,7]

Then, 24 round test specimens of 16.2 dm diameter (total surface area: 4.56 in^2) were cut from each silicone rubber sheet and they were rinse twice with Milli-Q water. Thereafter, they were extracted with 100 ml of Milli-Q water at reflux temperature for 7 hours. After the extraction, the solvent was decanted into a previously tared falcon, which was lyophilized and weight afterwards. Meanwhile, the specimens were placed in the oven at 40 ºC and dried until constant weight was reached. Then, the same test article was again covered with the same volume of Milli-Q water and extracted at reflux temperature for 2 additional hours. After the extraction, the total extractive yield was one more calculated from the obtained lyophilizate residue.

3.2.3.2. Migration into n-hexane.

4.56 in^2 test specimens were prepared on the very same manner as previously described and after, they were rinsed twice with Milli-Q water. Then, they were covered with 100 ml of n-hexane and extracted at reflux temperature for 7 hours. After the extraction, the extracts were cooled to room temperature, the silicone material was removed from the extracts, the solvent was concentrated on a rotary evaporator, and it was decanted into a previously amber glass container. Subsequently, both glass containers and tested specimens were placed into an oven at 40 ºC and they were dried to constant weight. Then, the same test article was again covered with the same volume of n-hexane and extracted at reflux temperature for 2 additional hours. After the extraction, the total extractive yield was one more calculated from the obtained dry extract.

3.2.4. <u>Qualitative analysis of the migration residues by GC/MS.</u>

External standards and sample test solutions were prepared as follows for the GC-MS analysis.

- Standard preparation: 3000 µl·l-1 D4 and D5 concentrated solutions were prepared by accurately measuring 30 µl of each standard and transferred to 10 ml sized volumetric flask which was then broad to volume with n-hexane. Then, 300 mg·l-1 D4 and D5 standard solutions were prepared from their concentrated solutions by taking 105 µl and 104 µl aliquots, respectively, and then broad to 10 ml with n-hexane.

- Sample preparation: Approximately 500 mg·l-1 sample test solutions were prepared from each of the recovered migration residues into n-hexane as follows: First, residue was reconstituted with 2 ml of n-hexane. Thereafter, 250 µl aliquot per each 100 mg was accurately measured and transferred to 25 ml sized volumetric flask which was then broad to volume with n-hexane.

GC-MS analysis was performed using an Agilent 6890 N gas chromatographer equipped with an Agilent 5975 B mass selective detector (MSD). The operating parameters were set as specified in the following table 3.1:

[Table 3.1]: GC-MS operating parameters. [8]

6890-N-GC	
GC Column	HP-5MS from J&W Scientific (30 m x 0.25 mm i.d, and 0.25 µm film thickness)
Oven temperature	40 °C (4 min) → 4 °C·min-1 up to 60 °C → 15 °C·min-1 up to 150 °C (5 min) →10 °C·min-1 up to 300 °C (30 min)
Total run time	65 min
Carrier gas program	He at a flow rate of 1.2 ml·min^{-1} (constant pressure mode)
Inlet program	Split mode (12.4:1), at a split flow of 14.9 ml·min^{-1} Inlet temperature: 300 °C
Injection volume	2 µl
5975-B-MSD	
Ion source	Electron ionization (EI) mode at 70 eV
Transfer line temperature	280 °C
Source temperature	230 °C
Quadrupole temperature	150 °C
Solvent delay	2.00 min
Acquisition mode	Full SCAN (m/z: 75-700)

Specially care was taken to minimise cross contamination problems that would likely result from siloxane's leaching out from column's stationary phase when it was heated. On this sense, previously carrying out the analysis the oven was heated at 260 °C for an hour. Afterwards, the suitability of the test was assessed by analysing and instrumental blank and a n-hexane blank.

Finally, sample test and standard solutions were injected twice. Between injecting different sampling extracts, n-hexane procedure blanks were also injected for cleaning the column.

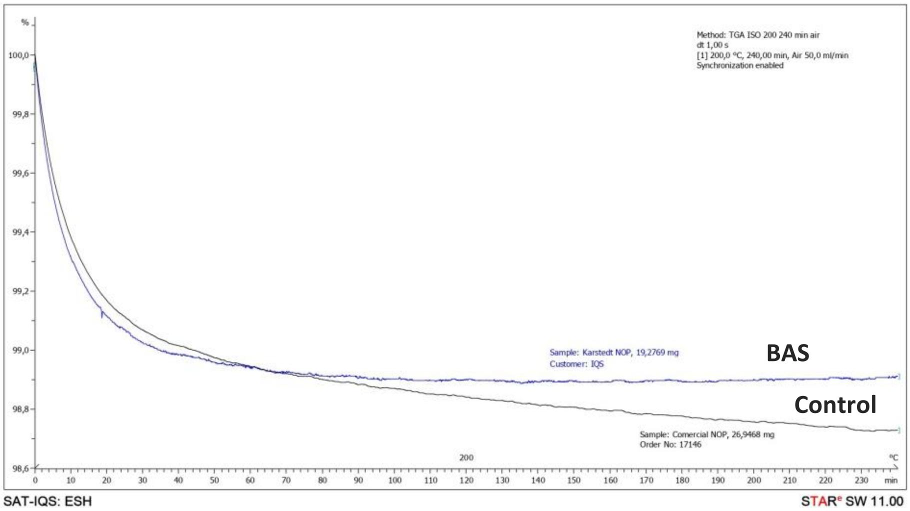
Qualitative dentification of migration substances was achieved by comparing their mass spectre to ones of filter candidates in the NIST library that reach at least a 90 % match with regards the ratio of main analyte’s ions. In each residue tested, all migration substances were semi-quantified by calculating the average response factors of the two standard solutions.

3.3. Results and discussion.

3.3.1. Catalysts effect on silicone elastomer’s weight loss over post-curing step.

The weight loss from both commercial (control) and BAS cured silicone materials has been monitored by TGA.

Results obtained are shown below:



[Figure 3.2]: Weigh loss in commercial silicone rubber (black curve) and BAS cured silicone rubber (blue curve) during post-cure heating.

[Table 3.2]: Summary of TGA results showing the effect of catalyst on silicone rubber’s weight loss during post-curing heating.

Sample	$\mathrm{Wt}_{\mathrm{loss}}(\%)$
Control	1.26
BAS	1.11

From isothermal thermograms shown in Figure 3.2, it is apparent that post-cure heating of the silicone rubber compounded with the developed catalyst results in a weight loss as well. Moreover, both platinum-cured silicone materials lost similar amounts of mass (table 3.2). However, it is noteworthy that when used the BAS’s catalyst the weight loss is stabilized, whereas with the commercial catalyst not. Which also indicates that the developed catalyst might have better performance on fixing low molecular weight silicone oligomers than the one of commercial.

3.3.2. Migration tests into food simulants.

As stated before, the suitability of new platinum-cured silicone material for extrusion applications used in food and beverage industry was studied with reference to FDA 21 CFR 177,2600 standard. Migration tests for both not post-cured (NP) silicone rubber and post-cured one (P) were performed as described in the methods section. Commercial silicone rubber's tests were also performed as reference.

Total extractive yield (TEY) results are reported on the following tables 3.3 and 3.4:

[Table 3.3]: Migration into Milli-Q water.[a]

Sample	W_0 (g)	7 h Residue (mg)	TEY	TEY <20 mg·in^{-2}	2 h Residue (mg)	TEY	TEY <1 mg·in^{-2}
Control	7.147	< 1	< 0.22	✓	< 1	< 0.22	✓
BAS	7.527	< 1	< 0.22	✓	< 1	< 0.22	✓

[a] Post-cured silicone rubbers were not assayed because of the very low migrating substance's content in not post-cured elastomers. In fact, submitted not post-cured materials do already comply with FDA requirements for aqueous FCM since their TEY values do neither exceed 20 mg·in^{-2} after the 1st extraction test nor 1 mg·in^{-2} after the 2nd extraction test.

[Table 3.4]: Migration into n-hexane.

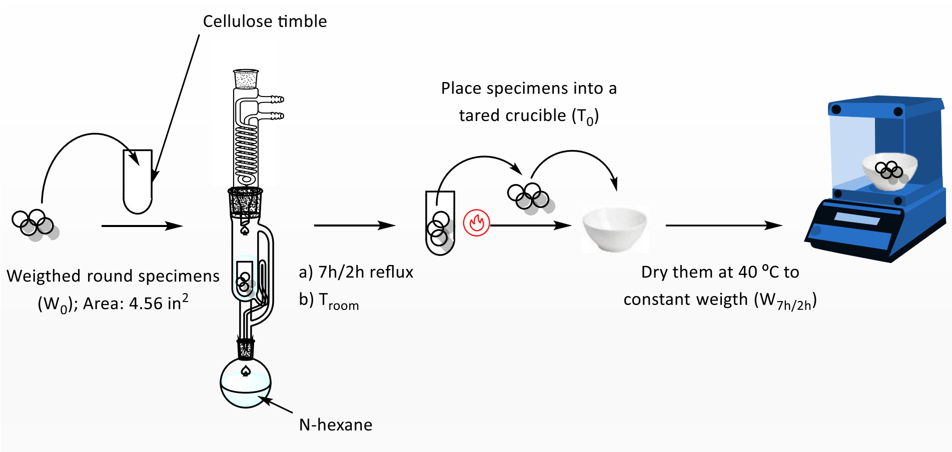
Sample		W_0 (g)	7 h Residue (mg)	TEY	TEY <175 mg·in^{-2}	2 h Residue (mg)	TEY	TEY <4 mg·in^{-2}
Control	NP	7.335	214	46.9	✓	20.5	4.5	✗
	P	7.137	118	25.8	✓	8.9	2.0	✓
BAS	NP	6.939	217	47.5	✓	23.2	5.1	✗
	P	6.790	117	30.0	✓	8.5	1.9	✓

As it can be seen, residues were only recovered at quantifiable amounts from n-hexane reflux extraction tests. Furthermore, TEY results denotes that with the new platinum-cured silicone rubber the same amount of total extractable compounds is obtained as when used the commercial catalyst for the curing.

Regarding to 21 CFR. 177,2600 requirements, both tested silicone elastomers either if were post-cured or not successfully passed the 1st extraction test because their resulted total extractive yields were far below the max. permissible value. However, only when silicone materials were thermally treated through a post-curing process, the total extractive yield from the 2nd reflux extraction did not exceed the limit of 4 mg·in^{-2}, whereas the TEY from not post-cured silicone materials exceed for very little the permissible value.

These results denote that only by post-curing platinum-cured silicone rubber it can be ensured that nothing in this material in the service will escape into the operational environment, preventing potential problems resulting from silicone cross-contamination, fogging, etc and thus make it suitable for being use in contact with foodstuff.

In order to better understand the reason from which not post-cured silicone materials fails to pass the 2nd extraction test, n-hexane migration tests were repeated using a Soxhlet apparatus (Figure 3.3):



[Figure 3.3]: Soxhlet extraction of silicone rubber samples. After the end of each extraction, TEY per elastomer's square inch was calculated from silicone rubber's mass loss (Wt_{loss}) instead of from mass of the residue recovered.

The advantage of applying Soxhlet extraction technique instead of the one of reflux extraction, relays on the continuous renewal of solvent in contact with the sample. This allows for an increase on extractive yield since the solvent is never saturated.

Total extractive yields obtained for not post-cured sample are shown in table 3.5:

[Table 3.5]: Overall migration from not post-cured silicone materials into n-hexane (Soxhlet extraction).

Sample	W_0 (g)	7 h			2 h		
		Wt_{loss} (mg)	TEY	TEY <175 mg·in^{-2}	Wt_{loss} (mg)	TEY	TEY <4 mg·in^{-2}
Control	7.147	273	59.9	✓	< 1	< 0.22	✓
BAS	7.527	280	61.4	✓	< 1	< 0.22	✓

Contrary to reflux extraction test, when Soxhlet extraction method was applied to samples, quantitative extractable removal from not post-cured silicone material was achieved after the 1st extraction. These results provide evidence that silicone rubber materials do not decompose upon heating them into boiling n-hexane, since otherwise a residue would also have been recovered after the 2nd extraction test. Thus, the recovered residue could only arise from residual volatile compounds already present in the silicone elastomer.

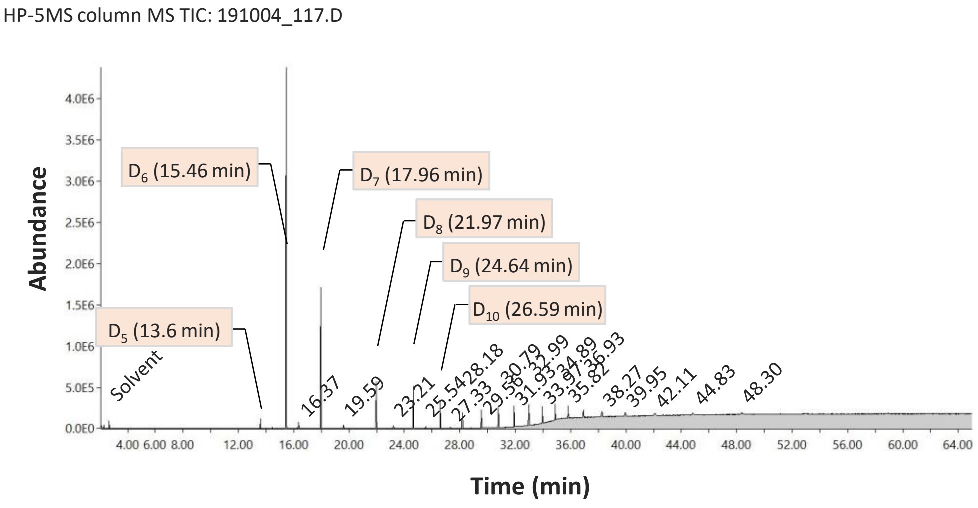
Furthermore, from the above observations it can be concluded that whether to meet or failing to pass FDA's requirements is determined by the methodology's sensibility used for performing such migration tests.

However, besides these conclusions, is still evident from the above migration tests that post-curing process has a great impact on the concentration of migrating compounds from platinum-cured silicone elastomer. So, we consider very important to characterize the compounds from the obtained residues in order to understand all the phenomena occurring during the post-curing process.

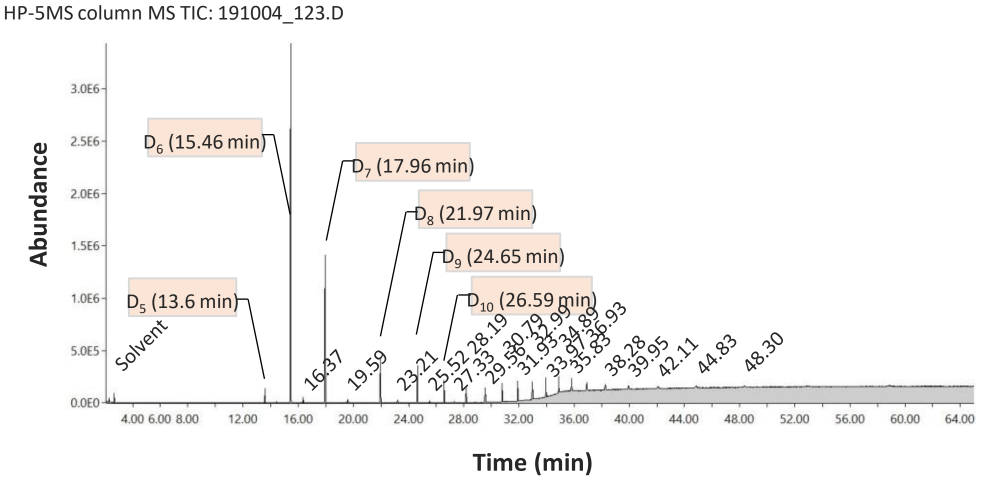
3.3.3. **Qualitative analysis of the migration residues by GC/MS.**

On these regards, approximately 500 mg·l^{-1} sample test solutions were prepared from residues recovered from FDA's migration test into n-hexane of both commercial silicone rubber and BAS cured silicone material, as described in the methods section, and then analysed by GC-MS.

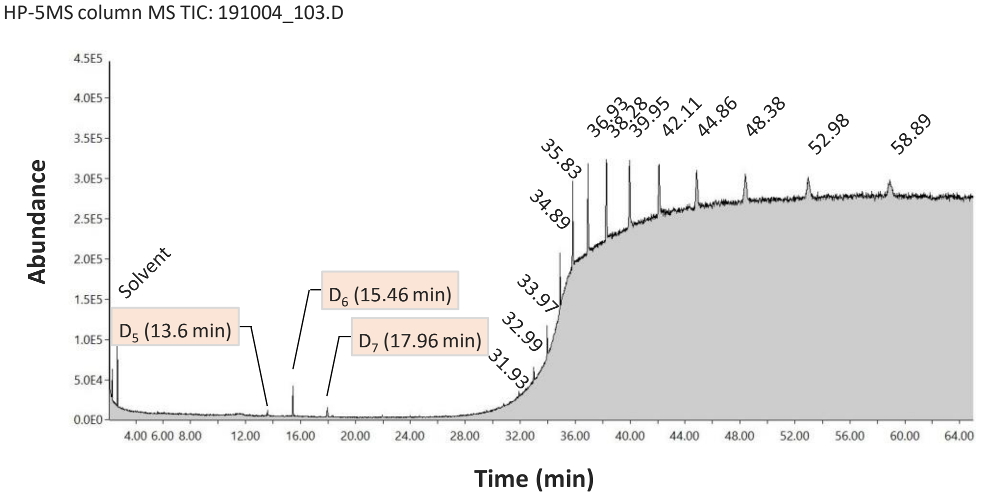
Results obtained are shown below:



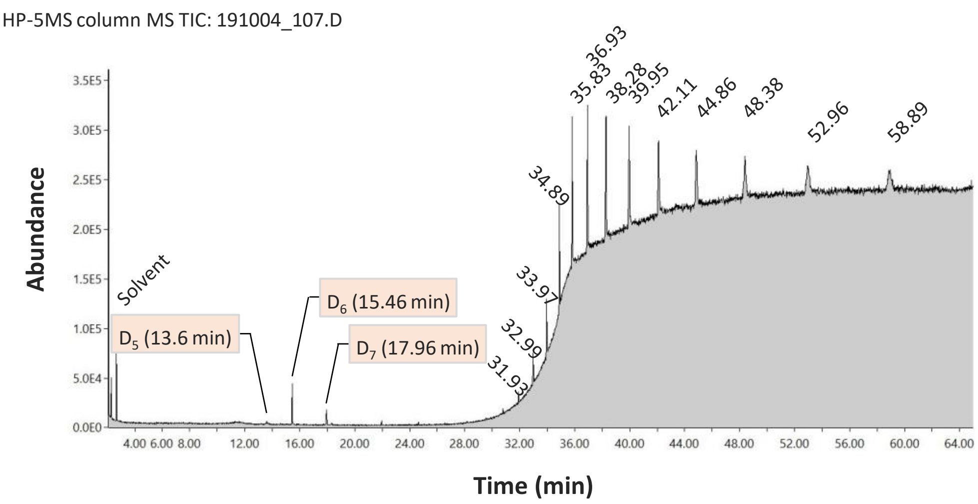
[Figure 3.4]: GC/MS chromatogram of n-hexane extract of not post-cured commercial silicone rubber.



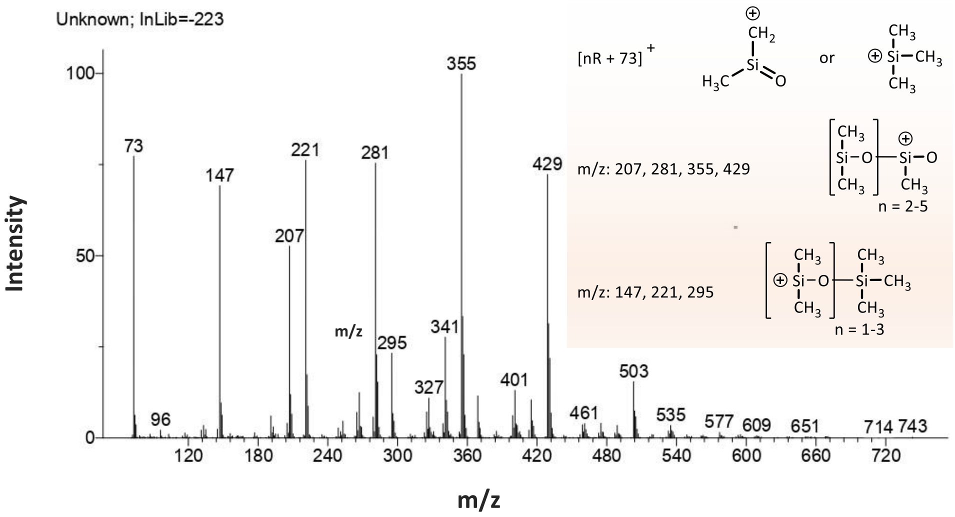
[Figure 3.5]: GC/MS chromatogram of n-hexane extract of not post-cured BAS cured silicone material.



[Figure 3.6]: GC/MS chromatogram of n-hexane extract of post-cured commercial silicone material.



[Figure 3.7]: GC/MS chromatogram of n-hexane extract of post-cured BAS cured silicone material.



[Figure 3.8]: A representative EI mass spectre example for linear siloxanes extracted from not post-cured silicone materials.[9]

[Table 3.6]: Extractables of both silicone materials detected by GC-MS in the n-hexane extracts as well as their estimated amount in µg released from 1 g of silicone material.

Sample	Total amount released (µg·g^{-1})			RT (min)
	NP	P	Compound	
Control	15545.1	131.5	Cyclics	13.6; 15.46; 17.96, 21.97, 24.64; 26.59
	5483.5	3316.3	PDMS fragments	16.37; 19.59; 23.21; 25.54; 27.33-48.30
BAS	14152.0	144.6	Cyclics	13.6; 15.46; 17.97, 21.97, 24.65; 26.59
	4710.0	4921.0	PDMS fragments	16.37; 19.59; 23.21; 25.52; 27.33-48.30

GC-MS qualitative analysis of residues recovered either from not post-cured commercial silicone rubber or BAS-cured one (Figure 3.4 and 3.5, respectively), denotes that the extractables are primarily constituted in both samples by volatile cyclic oligomers D_6 ($(Me_2SiO)_6$) and D_7 ($(Me_2SiO)_7$). Aside from these unreacted monomers, less abundant linear siloxane oligomers were also found based on the analysis of ions on their recorded EI mass spectres (and example is shown in Figure3.8, the rest of them have been attached on the Annex). Contrary to the cyclic oligomers, these are not removed from the elastomer upon heating it during the post-curing process. For instance, most of the peaks detected in the chromatogram of not post-cured silicone materials' residues are also observed in the ones of post-cured commercial silicone elastomer as well as in post-cured BAS silicone rubber sample (Figure 3.6 and 3.7, respectively).

Moreover, the quantification results illustrated in Table 3.6, denotes that similar concentration of these extractable compounds were obtained regardless of the post-curing conditions applied to the silicone elastomer as well as the catalyst used for the curing. These results make evident that enhancing hydrosilylation catalyst's performance will not provide a solution for dealing with the economical and productivity drawbacks of post-curing platinum-cured silicone rubber. As result, it is needed to search an alternative approach to significantly reduce the content of volatiles already present in the raw material; so that, the obtained platinum-cured silicone rubber could meet with such strict overall migration limits stated by main food contact regulations.

On this regard, some promising results have been reported to be obtained for pre-treatment of silicone compounding parts before curing in the mold.[10] While other researches have been described the use of CO_2 cleaning technology as an effective non-toxic solvent for extracting volatiles and extractables from either part, or from the cured elastomer. [11] In the present work it was chosen to study the one of thermal pre-curing treatment of KE-561U silicone base due to its simplicity.

3.3.4. <u>Efficiency of thermal devolatilization of VMQ silicone base, prior to cure, as an alternative treatment to post-curing.</u>

As a first approach, it was proposed to heat KE-561 U silicone base at 200 ºC for 30 minutes prior to be compounded with the rest of parts based into the weight loss profile of platinum-cured silicone materials during post-curing (Figure 3.2). More specifically, silicone rubber tests samples were prepared as follows: Around 100.0 g of KE-561 U was weight and smooth out in the 2RMM to produce a sheet of approximately 2 mm thickness in order to ease heat flux throughout the polymer's area.

Then, the sheet was placed on a glassware baker and heat at 200 °C for 30 minutes on air-circulating oven. At the conclusion of 30 minutes, the baker was retired from the oven, and the raw polymer was allowed to cool down to room temperature. Thereafter, the silicone base was compounded with 2 phr of cross-linker agent (C-25 B) and 0.5 phr of platinum catalyst's silicone paste (C-25 A) in the 2 RMM up to obtain a homogenous silicone material sheet with approximately 2 mm in thickness. Finally, the obtained silicone material sheet was cured by compression molding at 120 °C (10 min, 40 MPa).

In order to establish if pre-treatment of silicone base under the proposed conditions is a viable alternative route to silicone rubber's devolatilization, the obtained platinum-cured silicone rubber must accomplish the following specifications:

- Overall migration into food simulants must not exceed FDA 21 CFR177.2600's limits.
- The mechanical response of the obtained silicone rubber must not significantly differ from the one obtained after the post-cure heating treatment.

3.3.4.1. Migration test into n-hexane.

Since the major content of volatiles was determined with the migration test using n-hexane, for this part of the work we will focus on this test. On this regard, two test specimens were assayed as described in the methods section. Overall migration test results are shown in the following table 3.7:

[Table 3.7]: Migration into n-hexane from commercial heat-treated silicone material.

Sample	W$_0$ (g)	7 h			2 h		
		Residue (mg)	TEY	TEY <175 mg·in^{-2}	Residue (mg)	TEY	TEY <4 mg·in^{-2}
1	7.748	183	40.1	✓	14	3.1	✓
2	7.645	184	40.4	✓	13	2.9	✓
Average TEY			40.2	✓		3.0	✓

As it can be seen when tested n-hexane reflux extraction, the submitted heat-treated silicone rubber does comply with FDA requirements for FCM rubber.

Moreover, when the sum of total extractive yield values from the heat-treated silicone rubber was compared with the untreated one, the amount of residue recovered from heat-treated material was reduced by almost a 20 % with regards the not post-cured one (43.2 mg·in^{-2} and 52.6 mg·in^{-2}, respectively).

This reduction may seem as modest, but it is noteworthy considering that the heating cycle has been reduced almost a 90 % with regards the one required for effective volatile siloxane removal from cross-linked rubber through a post-curing process.

3.3.4.2. Study of the effect of the heat-treatment applied on silicone elastomer's mechanical properties.

Commercial silicone rubber samples were prepared and treated as specified in the following table 3.8:

[Table 3.8]: Silicone rubber samples prepared.

Sample	Heating treatment applied	
Control	-	200 ºC, 4 h
NP	-	-
H	200 ºC, 30 min	-
H + P	200 ºC, 30 min	200 ºC, 4 h

All silicone rubber samples were prepared on the same day and their mechanical properties were measured under the same experimental conditions as specified in section 2.2.2.5 on chapter 2.

Then, the mechanical properties of silicone elastomer that had not been heat-treated but that had been post-cured at 200 ºC for 4 hours (control), were compared with elastomers which were heat-treated at 200 ºC for 30 min (H), heat-treated and then post-cured (H + P), as well as the ones obtained from silicone elastomer which were neither heat-treated nor post-cured (NP). Table 3.9 displays data recorded from each of them:

[Table 3.9]: ρ23ºC, IRHD, σ_{max} and ε_{max} measured from commercial silicone rubber samples at four levels of heating treatments conditions.

	Sample			
	Control	NP	H	H + P
$\rho_{23°C}$ ($g \cdot cm^{-3}$)	1.1554, 1.1552, 1.1551, 1.1551, 1.1539, 1.1528, 1.1524, 1.1534, 1.1549, 1.1527	1.1482, 1.1474, 1.1504, 1.1502, 1.1587, 1.1482, 1.1484, 1.1502, 1.1502, 1.1492	1.1563, 1.1534, 1.1525, 1.1516, 1.1529, 1.1519, 1.1513, 1.1511, 1.1542, 1.1541	1.1560, 1.1563, 1.1562, 1.1566, 1.1565, 1.1555, 1.1554, 1.1549, 1.1549, 1.1561
IRHD	64.1, 63.8, 63.3, 63.9, 63.8, 63.9, 63.8, 63.9, 64.0, 64.4	54.9, 56.2, 57.9, 58.2, 56.7, 55.8, 57.1, 56.5, 57.5, 56.4	64.5, 65.2, 64.5, 63.6, 64.1, 63.0, 64.5, 63.4, 63.8, 61.9	59.7, 59.7, 60.0, 60.6, 60.1, 60.2, 59.7, 58.8, 59.0, 58.8

	Sample			
	Control	NP	H	H + P
σ_{max} (MPa)	10.16, 11.21, 10.45, 10.44, 10.69, 9.74, 10.19, 10.53, 10.66, 9.71	10.03, 10.12, 10.65, 10.22, 10.85, 10.16, 10.48, 9.73, 9.82, 9.93	9.97, 9.35, 9.65, 9.20, 10.82, 9.68, 10.38, 10.86, 9.86, 9.76	10.30, 9.88, 9.95, 10.14, 10.48, 10.21, 10.46, 10.31, 10.26, 10.26
ε_{max} (%)	346, 402, 363, 366, 361, 334, 353, 384, 384, 380	497, 446, 471, 504, 502, 476, 488, 413, 413, 414	418, 393, 422, 331, 434, 396, 416, 441, 410, 397	359, 334, 367, 362, 362, 332, 360, 367, 380, 376

Differences between the means values for density, hardness, tensile strength, and stress-strain measurements were assessed at a 1% significance's level by performing a one-way ANOVA. Descriptive statistics and ANOVA test results are summarised in the following table 3.10 and 3.11, respectively:

[Table 3.10]: Descriptive statistics.

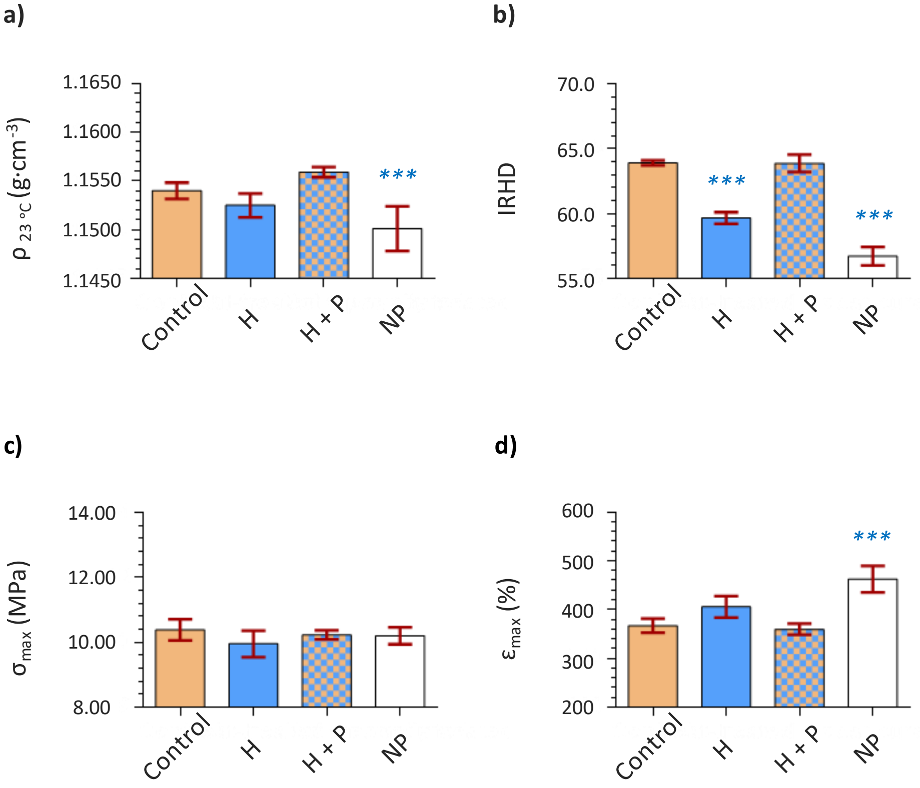
M ± SD	Type of heating treatment applied			
	Control	NP	H	H+P
$\rho_{23°C}$ (g·cm^{-3})	1.1541 ± 0.0012	1.1501 ± 0.0032	1.1526 ± 0.0017	1.1558 ± 0.0006
IRHD	63.9 ± 0.9	59.7 ± 0.6	56.7 ± 1.0	63.9 ± 0.3
σ_{max} (MPa)	10.38 ± 0.45	10.20 ± 0.36	9.95 ± 0.57	10.23 ± 0.19
ε_{max} (%)	367 ± 20	462 ± 38	406 ± 31	360 ± 16

[Table 3.11]: ANOVA table.

Variable	Variability's source:					
	Error		*Silicone's treatment*			
	MS	df	MS	df	F-test	p-value
$\rho_{23°C}$	$3.77 \cdot 10^{-6}$	36	$5.98 \cdot 10^{-5}$	3	15.9	< 0.001
IRHD	0.58	36	121.95	3	209.5	< 0.001
σ_{max}	0.17	36	0.31	3	1.8	0.17
ε_{max}	760.42	36	21998.03	3	28.9	< 0.001

According to ANOVA test's results (table 3.11), it is observed the effect of volatiles content in silicone material with regards its mechanical properties. For instance, significant higher IRHD average values were obtained in those silicone material samples which were post-cured (i.e., either control or H+P groups) than those which were not (NP and H). Whereas post-curing treatment leads to a softening effect on the recorded $\varepsilon_{\max}$ values (table 3.10).

In contrast the same average $\sigma_{\max}$ value was obtained regardless the treatment's conditions applied to the silicone material. These observations were confirmed when performed Dunnet's post-hoc test (Figure 3.9 a-d):



[Figure 3.9]: Silicone rubber's average mechanical properties as function of the heating treatment applied. a) $\rho_{23°C}$, b) IRHD, c) $\sigma_{\max}$, and d) $\varepsilon_{\max}$. Error bars indicates the 99 % CI of the mean and *** $p < 0.001$ using Dunnett's multiple comparison test, for comparison with control.

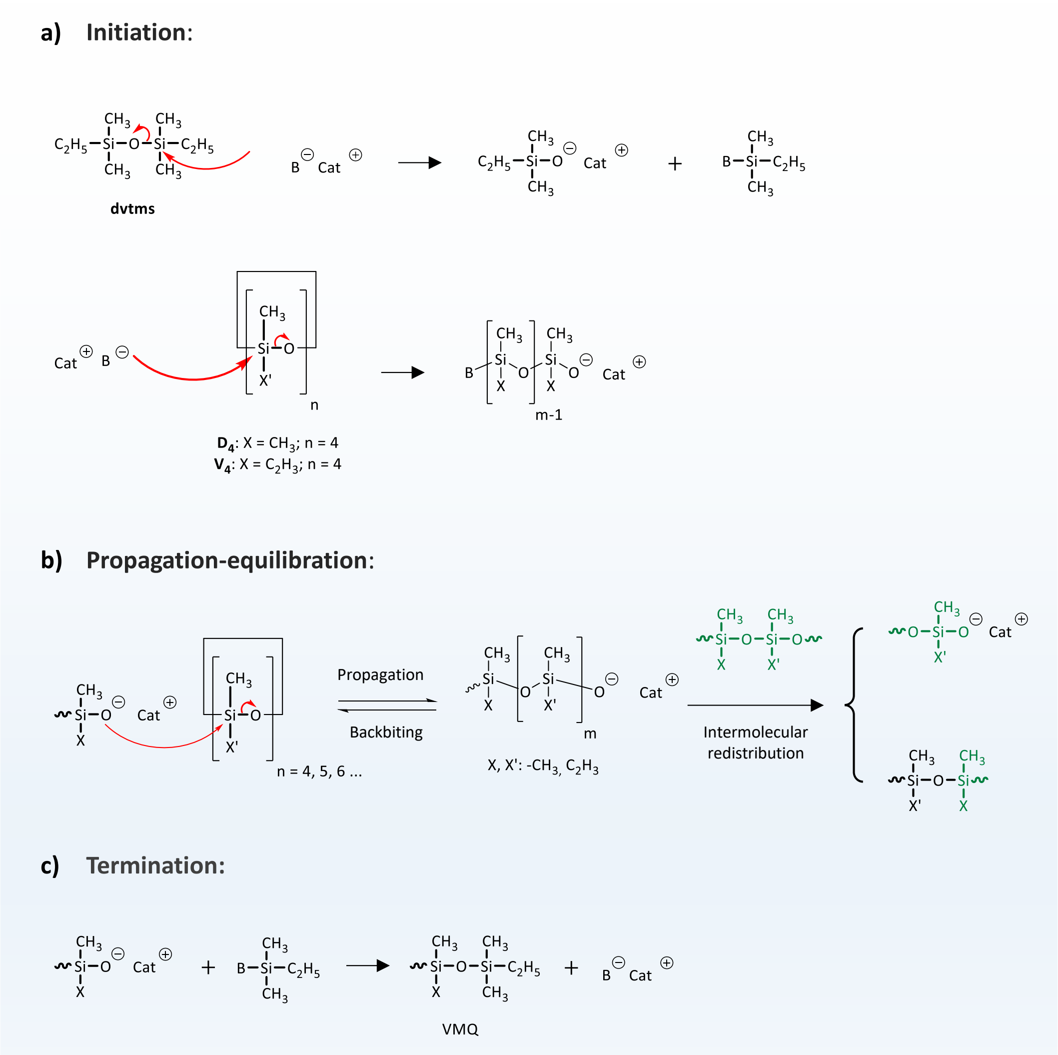
However, when comparing pre-treatment of KE-561U silicone base effect on elastomer's mechanical response with regards the one resulted from silicone material's post-curing, these differences are in most of the cases meaningless. For instance, there is no significant difference between the elongation at break mean values according to means 99 % confidence intervals' comparison (Figure 3.9, d) and the same is observed with density (Figure 3.9, a).

Only significant differences were detected in the case of hardness, but these differences might be arisen from the difference in volatile siloxanes' content on the treated materials, since low molecular weight siloxanes are well-known to act as silicone rubber's lubricants and thus, they might reduce its stiffness due to the increase on polymer network's free volume. Even so, their difference has not consistency in the practice if it considered Venair's acceptance criteria for KE-561 U post-cured silicone rubber's hardness, since the measured IRHD mean value falls within 60.0 ± 5.0 range.

3.4. Concluding remarks.

Studies performed in the present chapter showed that the post-curing processing does not entail a secondary cure of the silicone. It has been proved that there is a loss of weight due to the migration of oligomers and volatile compounds present in the gum.

Characterisation of these volatiles has been proved that silicone rubber's migrating substances are principally constituted by volatile cyclic oligomers. These might likely come as a result from anionic-catalized ring-opening copolymerisation of D_4 and V_4 (Figure 3.10 a-c), which is the main polymerisation method used in the silicone industry for large-scale manufacturing of VMQ silicone rubber gum stocks.



[Figure 3.10]: Overall scheme for D_4 and V_4 AROP, using dvtms as end-capping agent.[12,13]

This process gives at equilibrium cyclic oligomers plus functional silicone. The proportion of cyclic oligomers depends on several factors, but generally for a bulk polymerisation of dimethylsiloxane, the equilibrium concentration of cyclic oligomers might be as high as an 15 % of the polymer crude. Therefore, to provide a finished product these cyclic oligomers must be removed in vacuo. [14] This evaporation process though, might not fully remove these volatiles from silicone polymer and consequently, it is unavoidable expect some outgassing from the cross-linked elastomer if these are not first removed from the material by subjecting it to a post-cure heating treatment.

The release of these volatile siloxanes cannot be avoided by means of improving silicone addition-curing process, since such siloxane compounds do not play any relevant role during the curing reaction. The post-curing process has nothing to do with the enhancement of the mechanical properties, but with the quality of the silicone gum.

Thus, the catalyst activity cannot contribute to minimize the content of such compounds. The post-curing process then, is not meant to obtain a material with better mechanical properties, but simply a process to minimize the migration of oligomers and volatile compounds during the end use of the material. In this regard, a pre-treatment of the silicone gum before its use in the silicone elastomer formulation has been proved to be a promising devolatilization method for reducing volatile siloxanes already present up to a concentration into the silicone material well below the max. permissible levels stated by the FDA. Therefore, the application of the proposed alternative treatment means can obviate the need for post-cure devolatilization of cross-linked silicone material, and thus obtain a product with similar characteristics but, at a more competitive tubing's processing cost.

Once the post-curing stage of the silicone processing has been proposed to be substituted by a previous heating treatment of the gum, there is still another issue related with the cost of the production line that must be considered. Achieving a Pt catalyst with a superior TON/TOF ratio would be desirable in order to gain efficiency of the process. In this regard, despite the excellent stability results obtained there are still some features of BAS's catalyst that needs to be improved such as its catalytic activity as well as odor. Chapter 4 will present the optimization of the catalyst developed in Chapter 2.

3.5. References.

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Chapter 4: Novel Pt-based catalytic system for addition-curing silicones.

Chapter 4 has been intentionally excluded from the present work to preserve the confidentiality of commercially sensitive information provided in this chapter.

‘Se extingue el día, pero no el canto de la alondra.’

Matsua Bashō

Chapter 5: Conclusions.

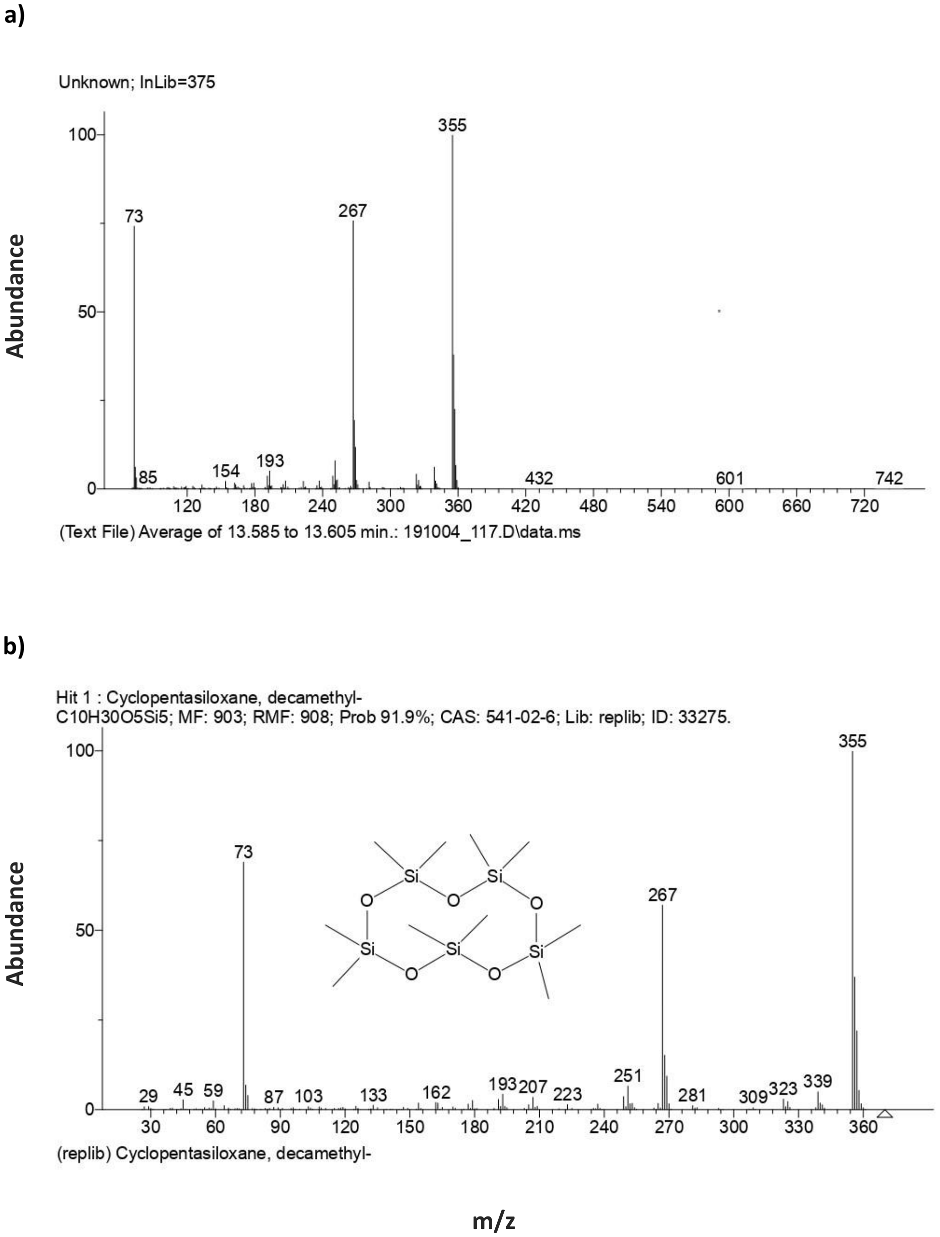
Different strategies have been explored during this work to deal with some aspects of addition-curing technology which results in lower productivity in sanitary silicone tubing's processing. In this regard, the following conclusions can be extracted in relation to the objectives set in the introduction chapter:

1. Concerning the catalyst technology developed, the following remarks are worth stating:
    - A robust one-step synthetic procedure has been developed which allows Venair to prepare a novel Pt catalyst, without requiring strict experimental conditions making it affordable and viable to be implemented within their production line.
    - More specifically, the addition of diallyl sulfide to Karstedt's catalyst has been proved to effectively prevent catalyst reductive deactivation into metal colloids without requiring the addition of any other external inhibitor. This fact improves the shelf-life of the catalyst, making it possible synthesize it in batches that can be stored without losing its properties.
    - Results obtained from preliminary scalability test suggest that the novel Pt/DAS catalytic system could be easily reproduced at a Kg-scale, which allows Venair Ibérica to guarantee its sanitary silicone hose production for two entire years without significant increase costs-associated with the catalyst. This know-how will make it possible for the company to gain more autonomy over its production lines and become less dependent from external suppliers.
    - The ne catalyst can be used without major modifications of the production line. Furthermore, no significant changes in the mechanical properties are detected.
    - The final product obtained with the new catalyst presents a better thermal degradation resistance due to the changes in the distribution of the crosslinks within the rubber matrix.
2. It has been found that the post-curing process that has been used until now in the production line of the company, did not aim to improve the mechanical properties of the final product. Thus, the post-curing process does not imply any process that has to do with the degree of crosslinking of the sample or with the kinetics of the reaction.
3. The post-curing process is being implemented in the company in order to fulfil the specifications of United Stated FDA 21 CFR177.2600 "Rubber articles intended for repeated use". However, it has been proved that this stage is exclusively related to get rid of the volatile compounds present in the material.

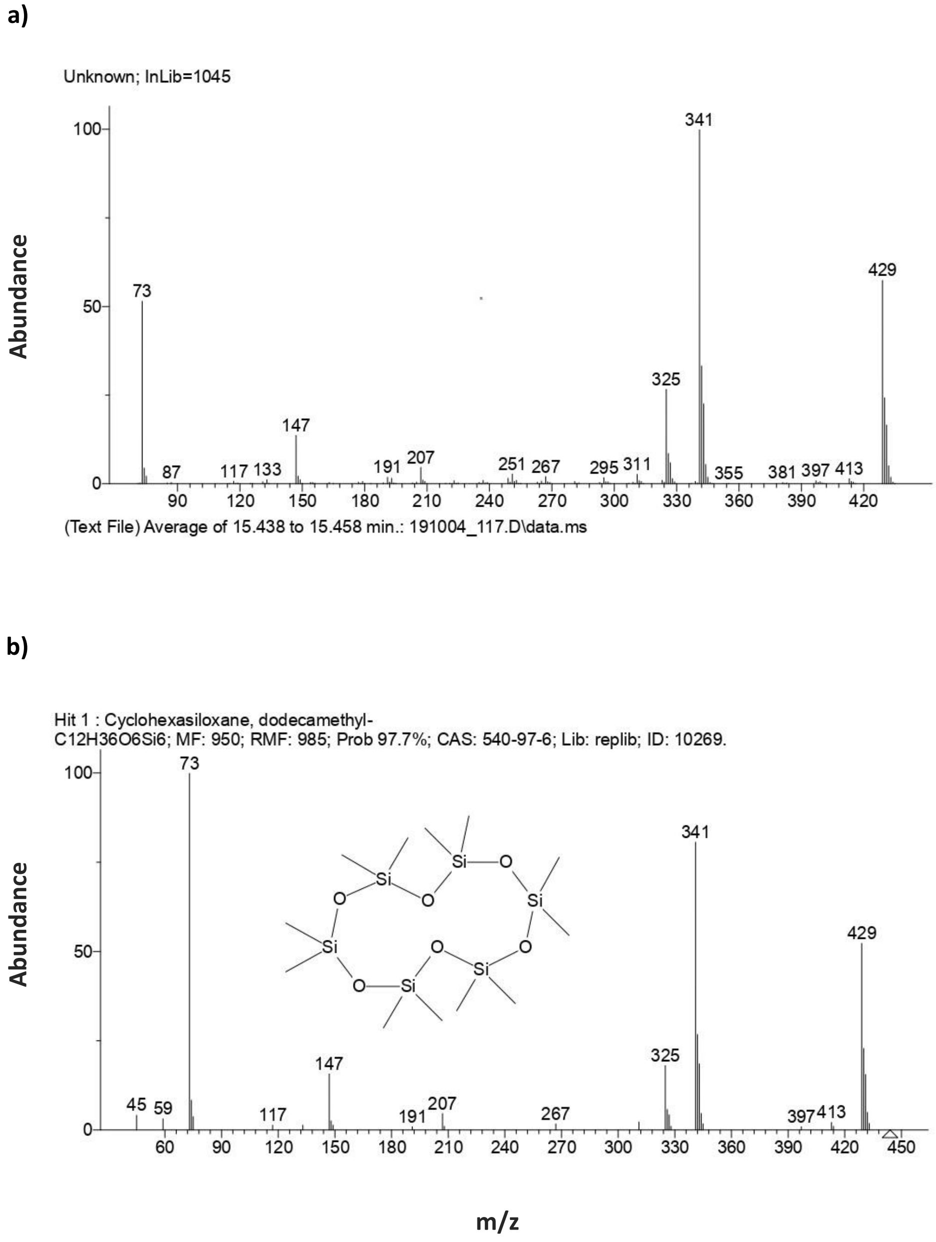
4. An exhaustive characterisation of the components that evolve during the post-curing process has been carried out, which has made possible to conclude that in all cases these are oligomeric and volatile compounds that come from the base rubber. These products are not actively involved in the curing process and therefore have no relation with the catalytic system used.
5. Instead of focusing on the catalyst to avoid this post-curing stage, a heat treatment has been proposed in order to remove products that may migrate to the surface of the tubes. Such treatment consists of applying a 30-minute thermal treatment to the silicone base before curing. This treatment has proved to be as an effective way to mitigate the need for a later 4-hour devolatilization step to comply with the migration levels stated by the FDA. This change in the production line implies a significant decrease on the production cost.

Appendix.

Identification of extractables from silicone elastomers:



Experimental (a) and bibliographic mass spectra (b) of D_5 cyclic siloxane.



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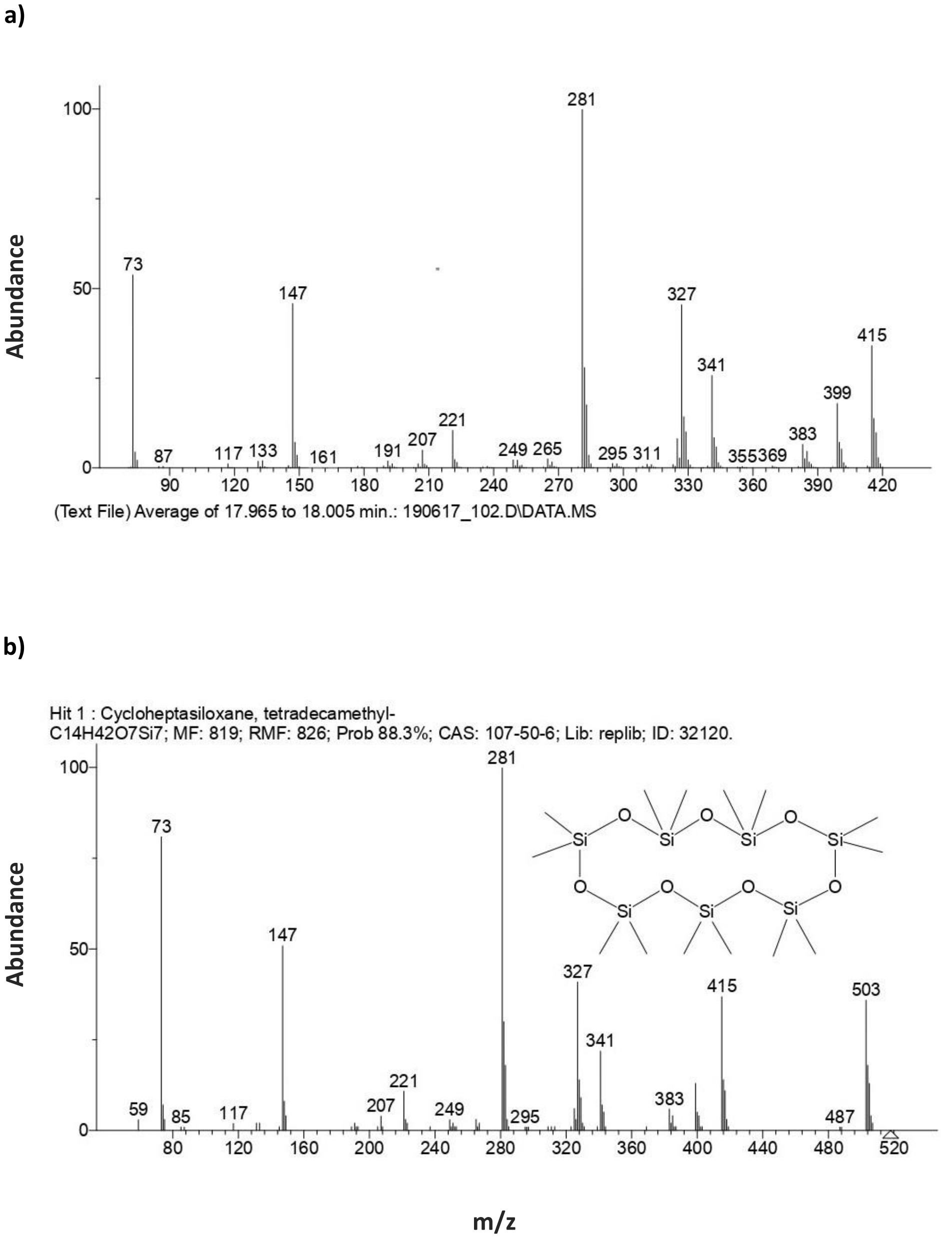

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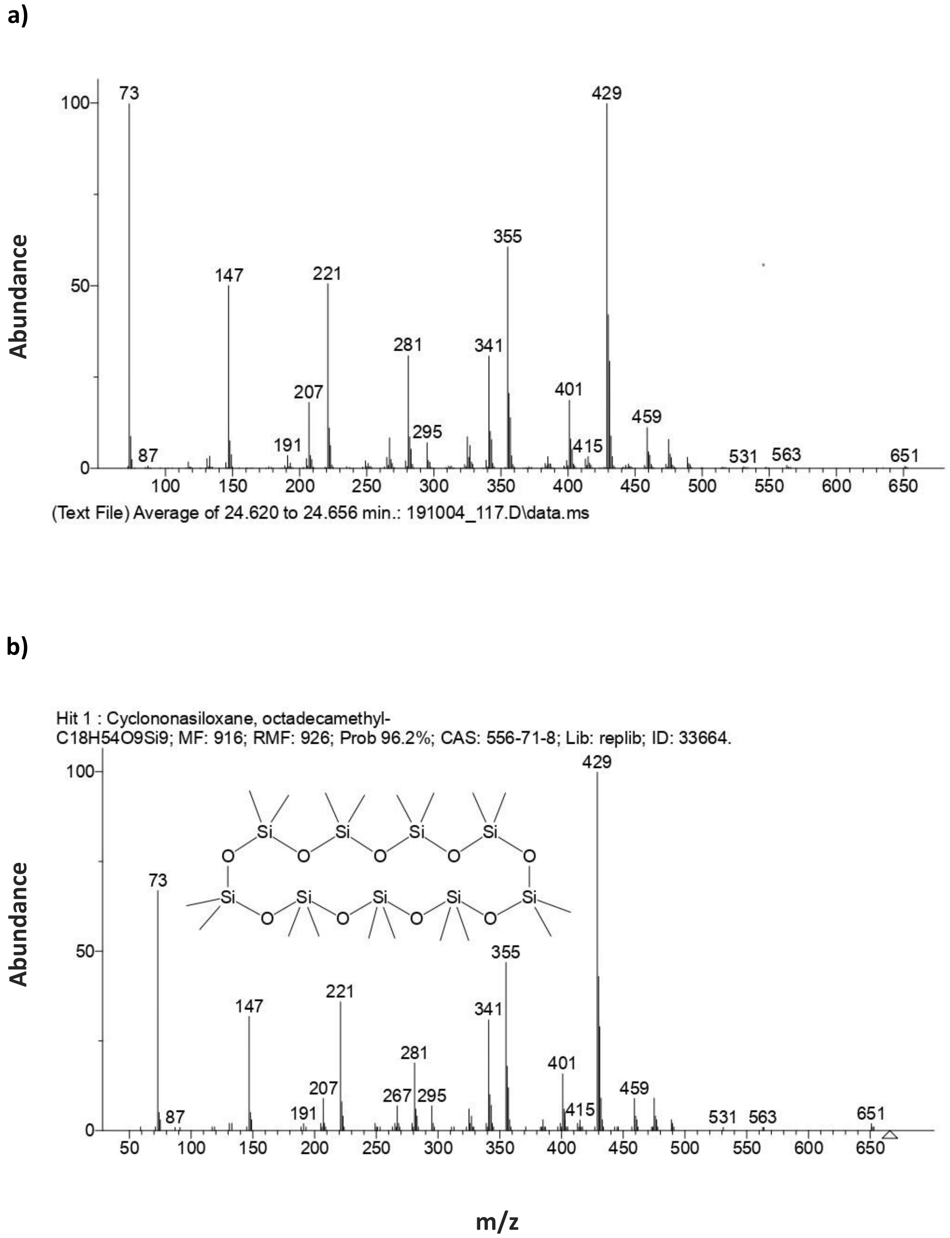

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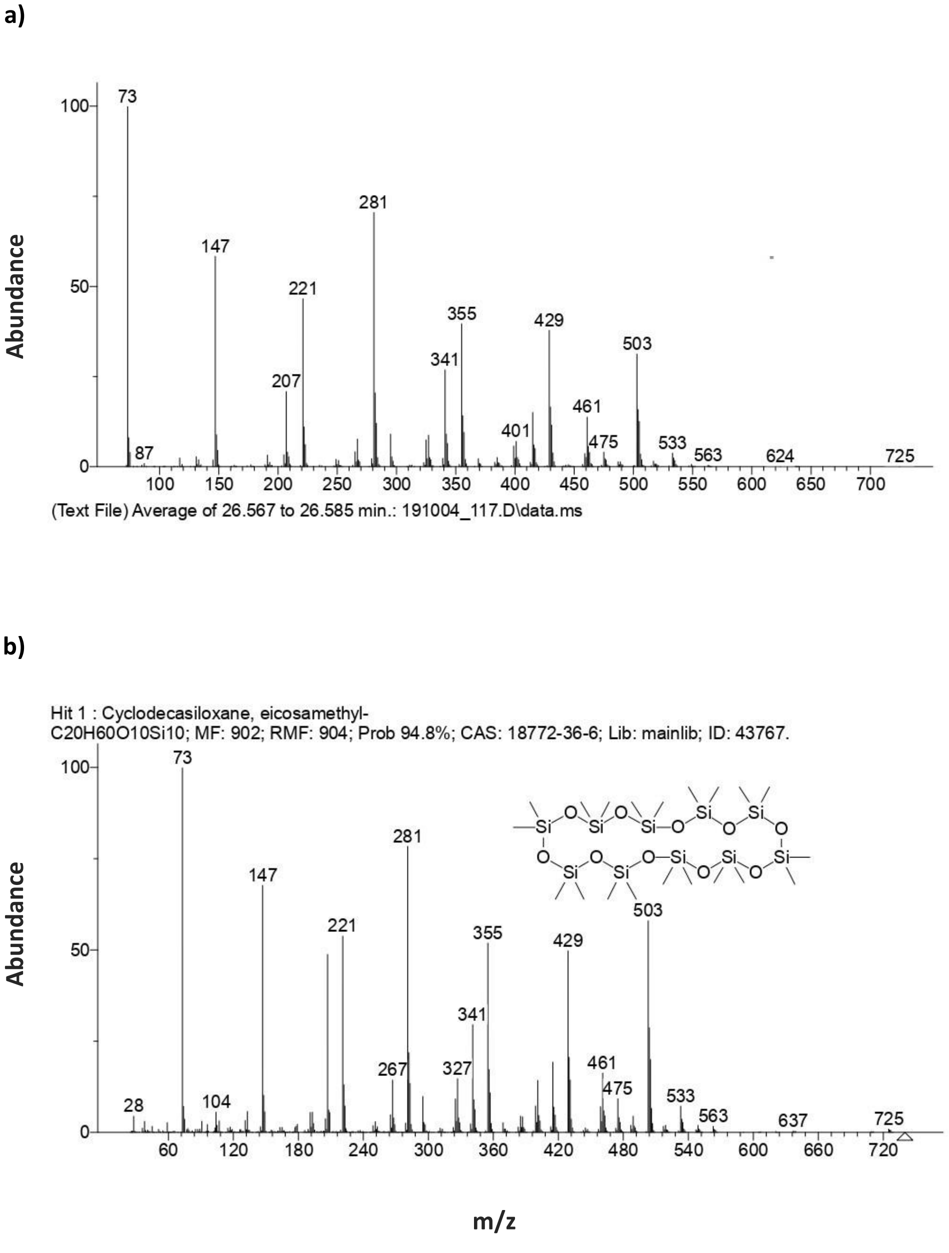

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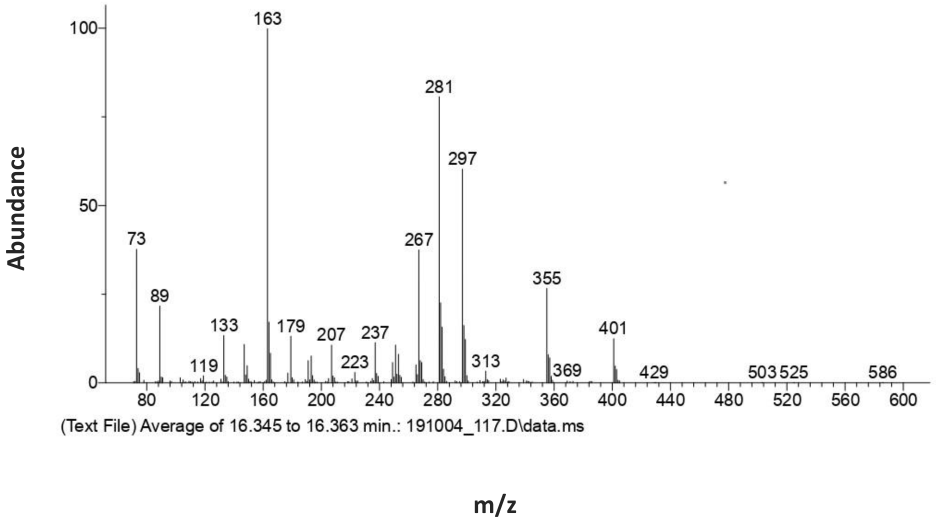

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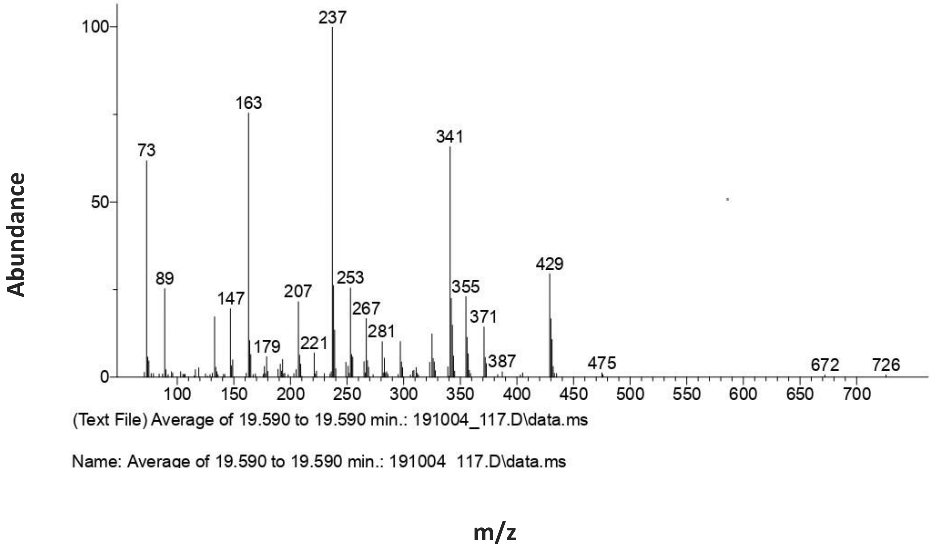

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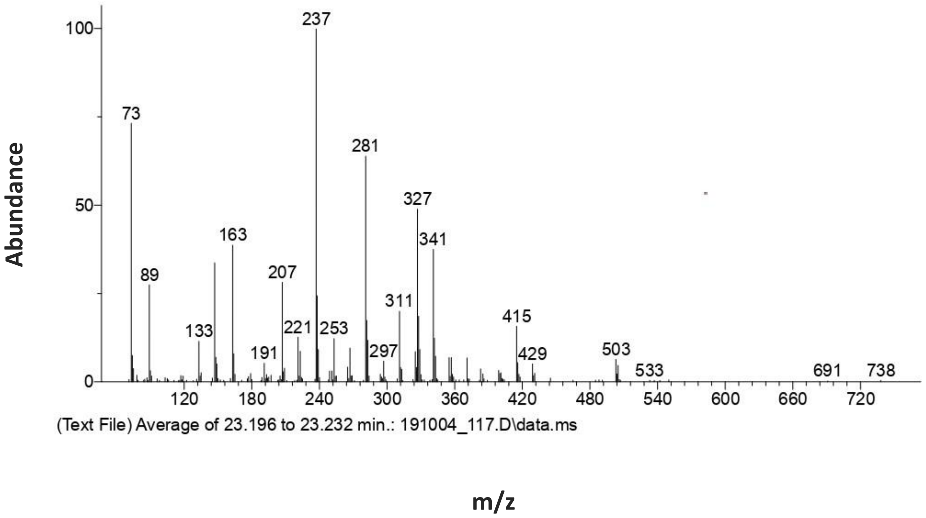

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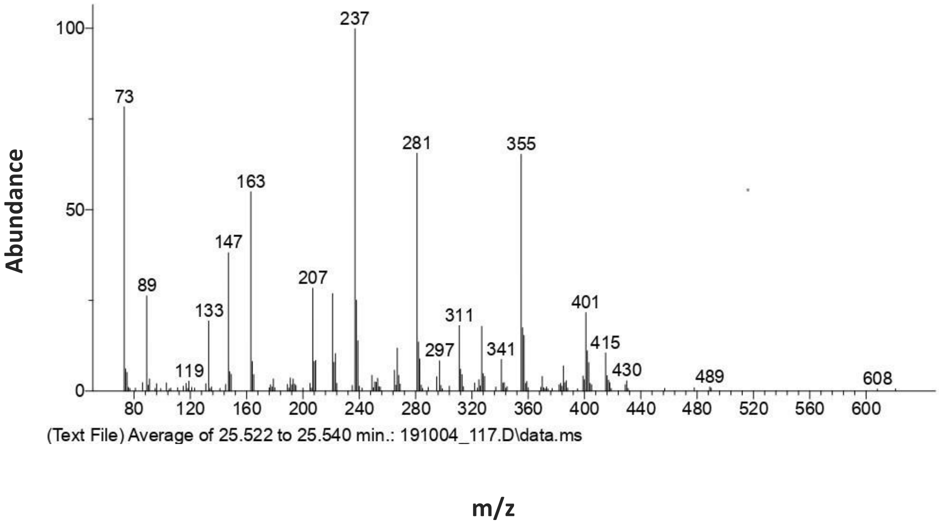

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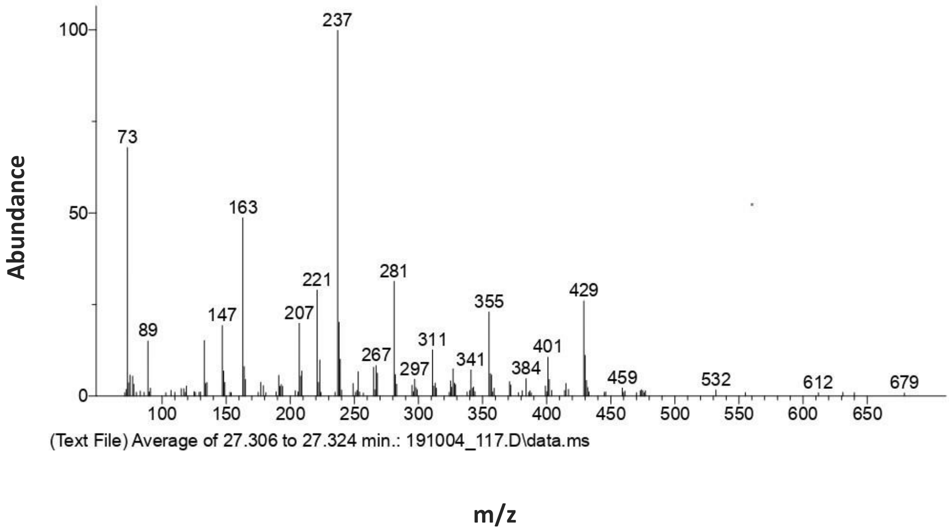

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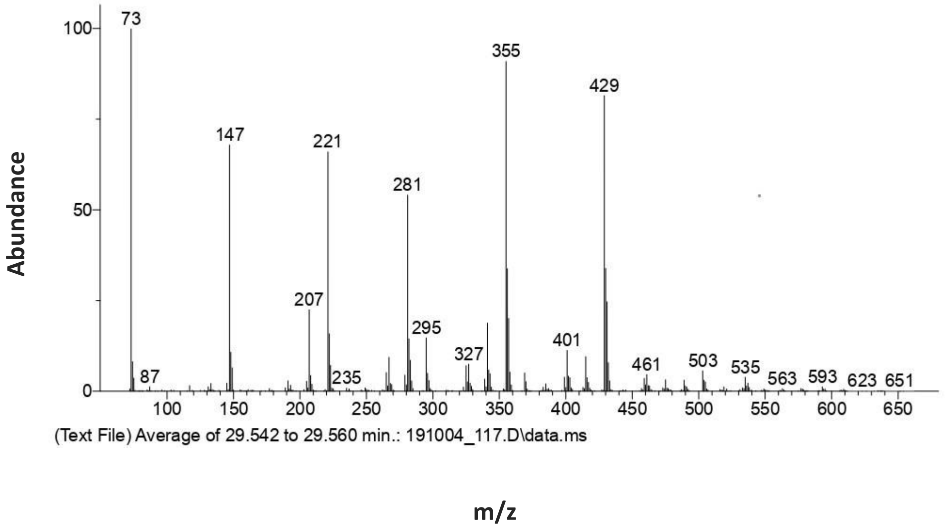

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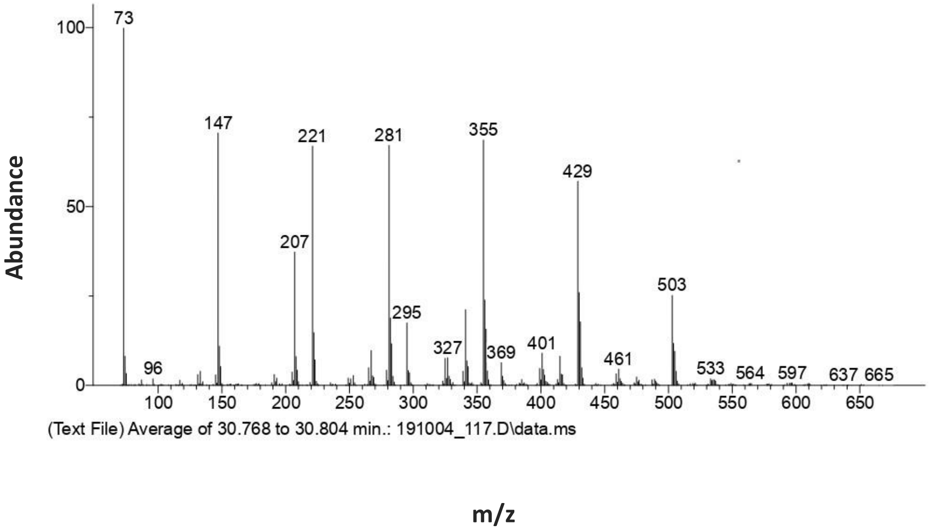

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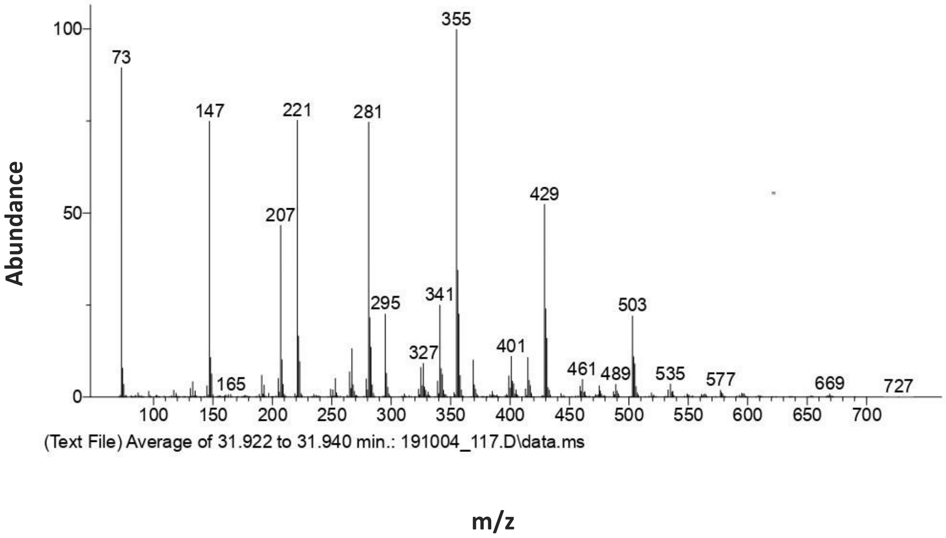
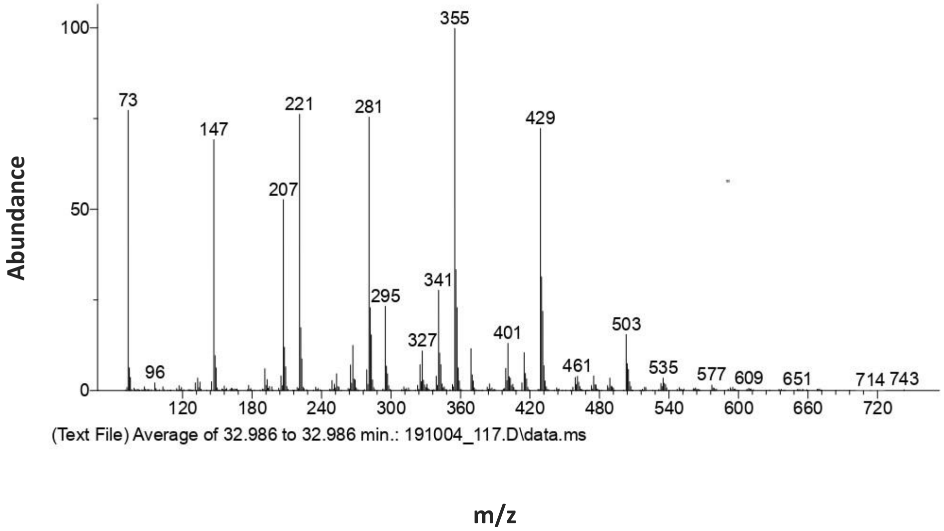


Linear siloxane (homologue series 1, m/z: 73, 147, 207, 221, 281, 341, 355, 429).



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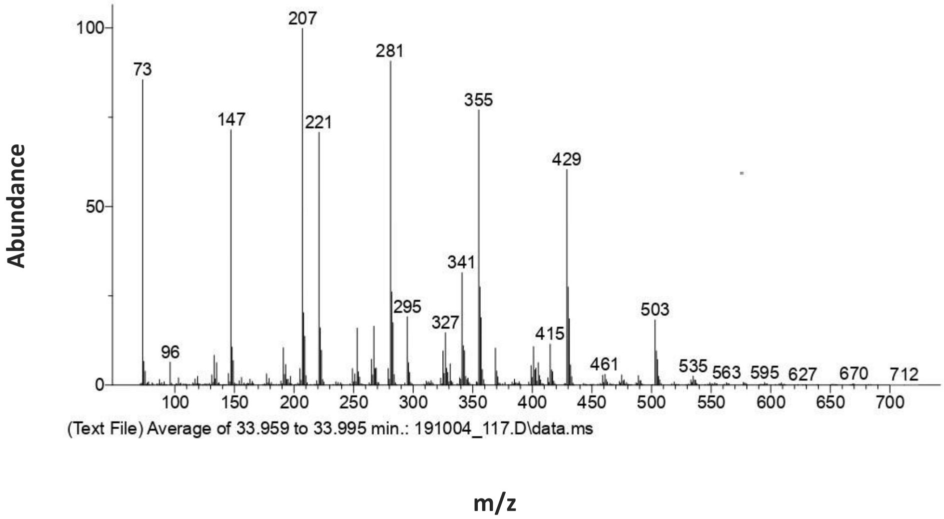

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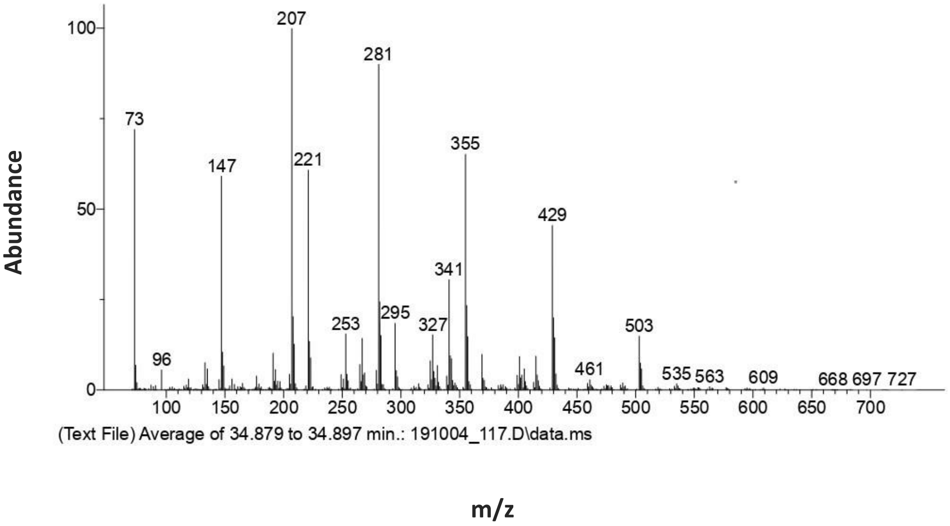

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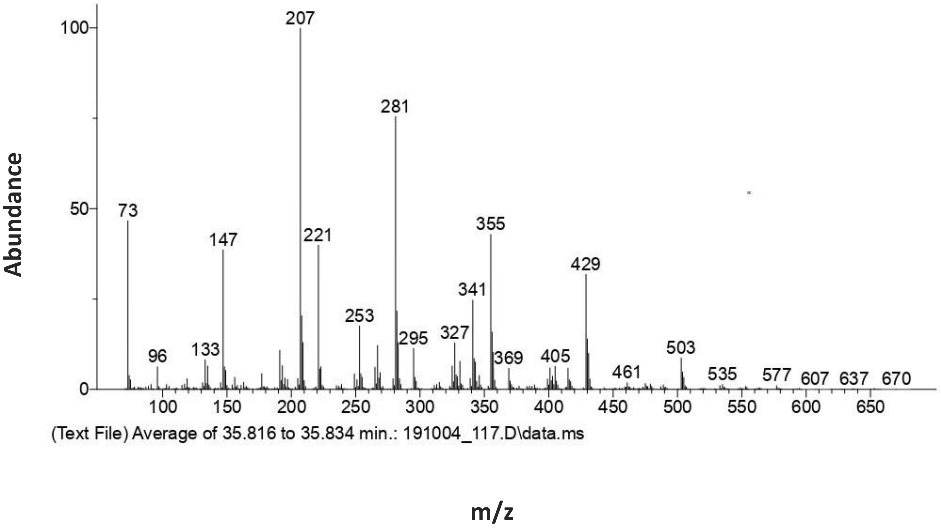

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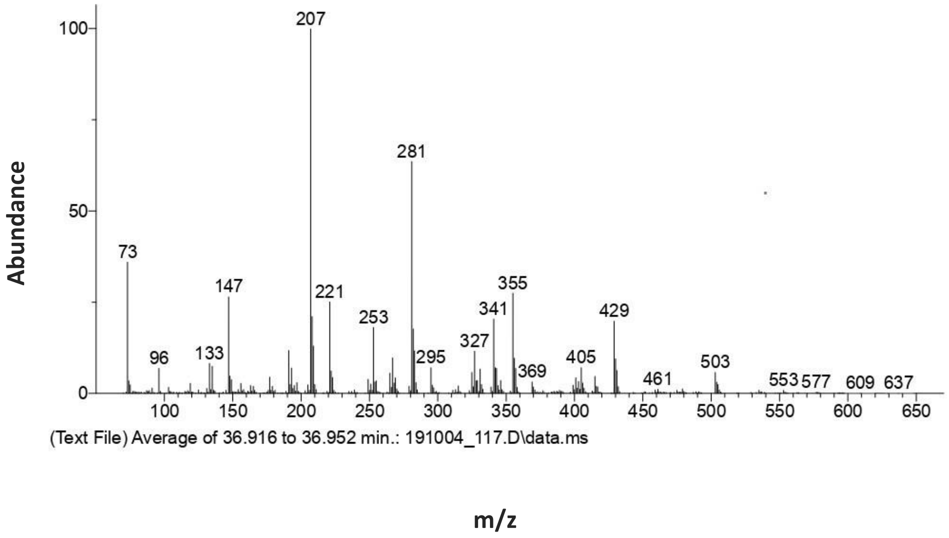

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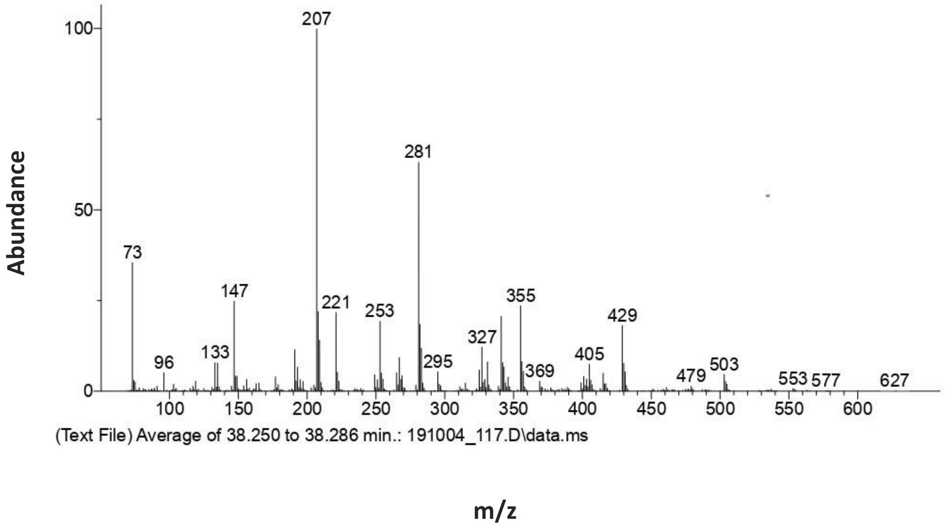

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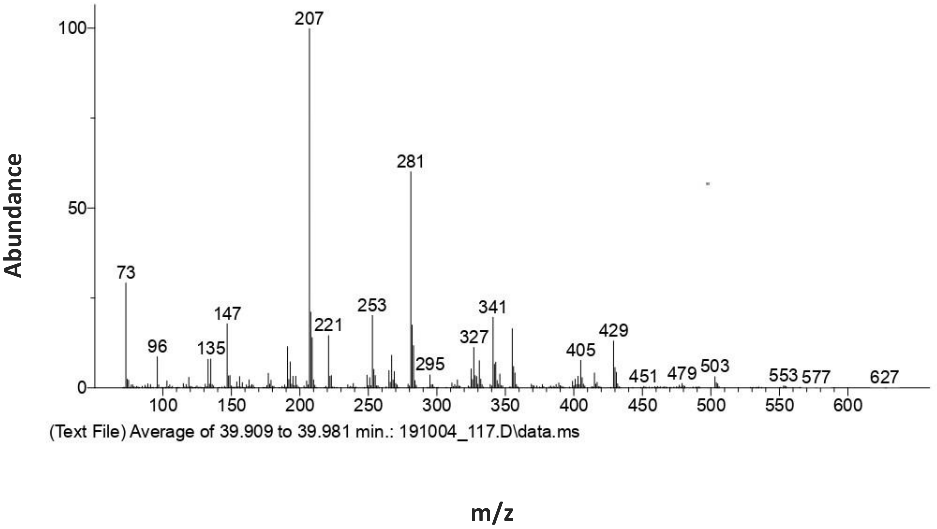

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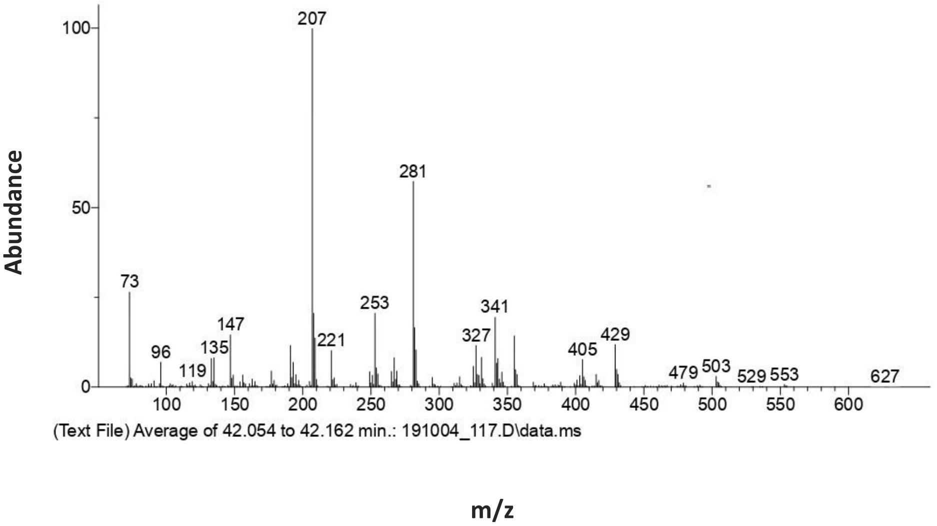

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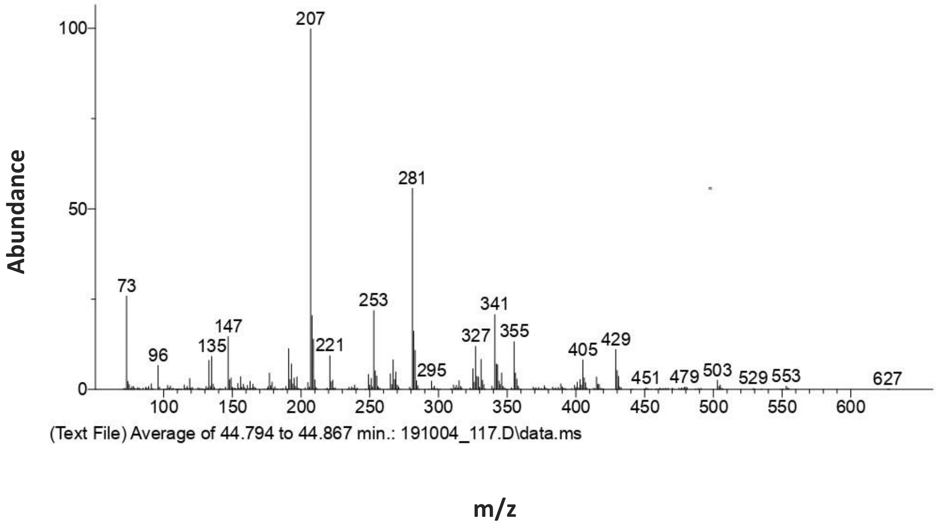

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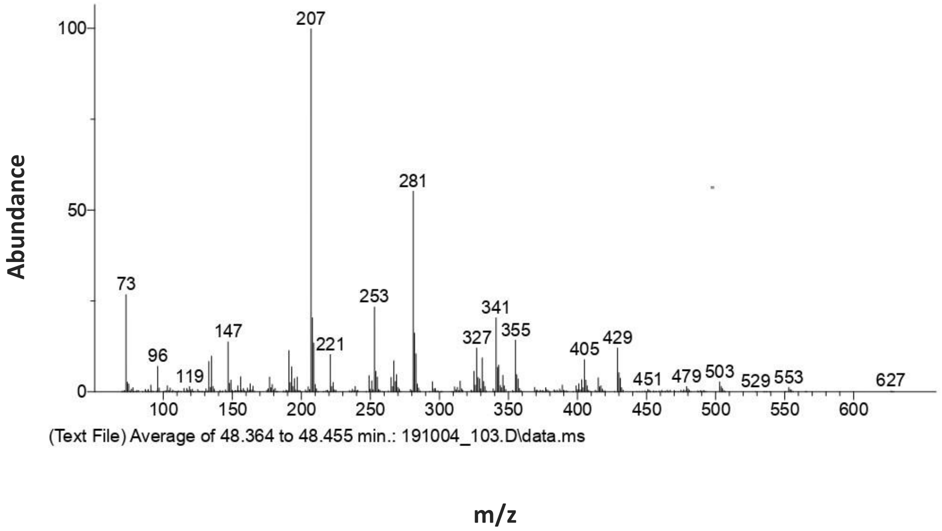

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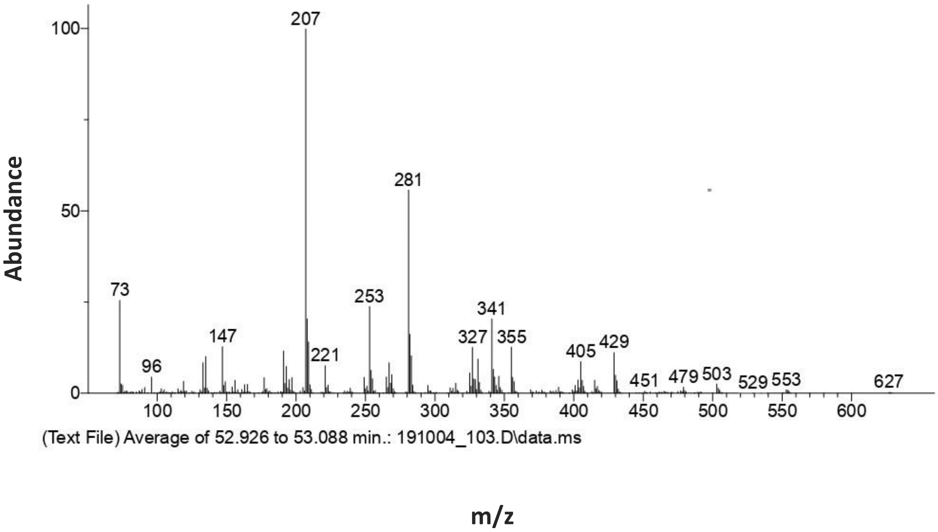

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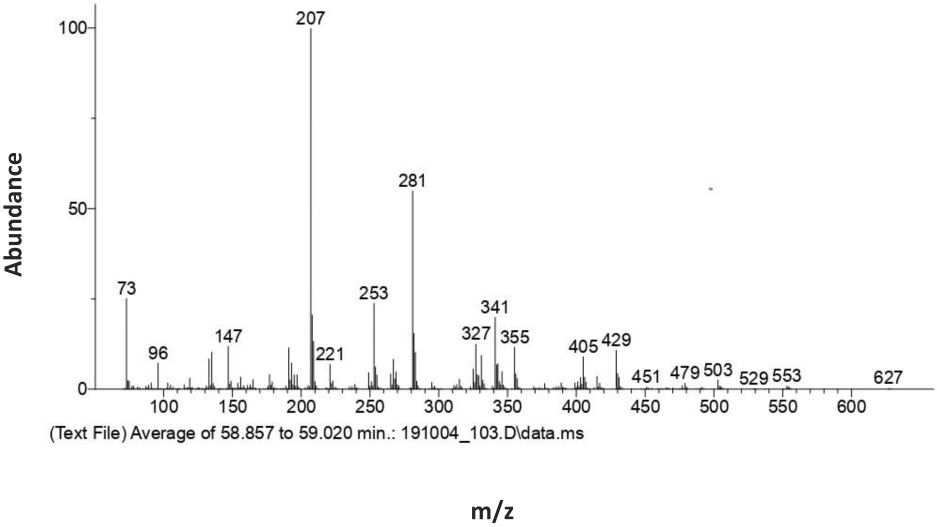

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