

Vacuum-Assisted Headspace Solid-Phase Microextraction for Enhanced Aroma Profiling of Fish Samples

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Diplôme : Master en bioingénieur : chimie et bioindustries, à finalité spécialisée

Année académique : 2018-2019

URI/URL : <http://hdl.handle.net/2268.2/8465>

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V. Annex

Annex 1: Distribution constant variation depending on temperature, salting, ph and matrix polarity.
(Pawliszyn Janusz, 1997)

<u>Parameter</u>	<u>Equation</u>	<u>Symbols</u>
Temperature	$K_{fh} = K_0 \exp \frac{-\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$	<p>T_0: initial temperature T: final temperature R: gas constant ΔH: molar enthalpy change of analyte when it moves from headspace to the fiber's coating. It can be approximated by the heat of vaporization of the pure compound. K_0: distribution constant at T_0</p>
Salting	$K_{fs} = K_0 e^{k_s C_s}$	<p>K_0: partition without salt C_s: salt concentration</p>
pH	$K = K_0 \frac{[H^+]}{K_a + [H^+]}$	<p>K_0: sample/fiber distribution constant when they are in their undissociated form. This parameter will only impact dissociable species and it is assumed that only the undissociated form will be extracted by the fiber.</p>
Polarity (solution with organic solvent)	$K_{fs} = 2,303 K_{fw} \exp \left(\frac{P_1 - P_2}{2} \right)$	<p>K_{fs}: pure water distribution constant $P_1=10,2$: water polarity $P_2=cP_s+(1-c)P_1$: solvent/water solution polarity. c: solvent concentration P_s: solvent polarity</p>

Annex 2: Example of QIM characteristics and associated score for the freshness study of bogue (*Boops boops*). (Bogdanovic & al., 2012)

Quality parameter	Description	Score
Appearance		
Skin	Very bright, iridescent	0
	Mat, deep colors	1
	Green-grayish, yellow near abdomen	2
	Grey, grey spots, bloody (near abdomen)	3
	None	
Blood on neck	None (0%)	0
	Some (1% to 50%)	1
	Much (51% to 100%)	2
Odor	Metal, species specific, seaweed, cut grass	0
	Neutral, slightly fatty, marine	1
	Brine, slightly off odors, stale dish cloth	2
Texture	In rigor	0
	Firm, elastic	1
	Less elastic, flexible, (finger mark disappears slowly)	2
Eyes		
Color	Transparent, bright	0
	Slightly opaque, filled with jelly fluid	1
	Opaque, bloody, yellow-white spots, filled with jelly fluid	2
Form	Convex	0
	Slightly convex to flat	1
	Sunken	2
Gills		
Color	Characteristic red	0
	Pale red, pink/slightly brown	1
	Pink, yellowish-brown	2
Odor	Metal, shellfish, slightly stale-smelling	0
	Neutral, boiled potato, slightly oily	1
	Oily, rusty	2
	Rancid, very sour off odor, cardboard rising damp, TMA	3
Vent	Shut	0
	Slightly open	1
	Open	2
Quality index (QI)		0-20

Annex 3: Work on fish volatiles in the literature.

n°	Ref	Method	Fiber	Sample size	Sample prep	Incubation	Temperature (°C)	Extraction time (min)	Analytical instrument
1		DHA (dynamic headspace analysis)	-	-	-	-	-	-	GC-MS
2		Gas sensor array	-	-	-	-	-	-	-
3 (A)		HS-SPME	CAR/PDMS (65µm)	11mL of supernatant	50g of sample + 100mL ultrapure water saturated with NaCl. Then centrifugation (12000g, 10', 4°C)	10 min at 50°C and 500rpm	50	40	GC-MS
4		HS-SPME	CAR/PDMS (75µm)	1g	(fish oil emulsion)	10 min at RT	60	30	GC-MS
5 (B)		HS-SPME	CAR/PDMS/DVB	no mention	Fillets	no mention	40	45	GC-MS
6		HS-SPME	PDMS (100µm)	20g + 25mL water (36% NaCl)	Reduced to powder	1h	40	15	GC-MS
7		HS-SPME	PDMS (100µm)	1g	(fish oil)	15 min at 150°C with 500 rpm	150	30	GC-MS
8		HS-SPME	PDMS/DVB (65µm)	2,5g	microencapsulated powder + 5g water saturated with NaCl + 0,5mL IS	no mention	80	45	GC-FID+ olfactory detector outlet
9		HS-SPME	PDMS/DVB	1g	Finely ground fillet + 3mL water 40% NaCl. Heated 20 min at 70°C	10 min	35	2	GC-NPD
10		HS-SPME	CAR/PDMS (75µm). Derivatization	6g	Sample + 6mL distilled water, homogenized	no mention	80	30	GC-MS

with PFBHA

11	HS-SPME	CAR/PDMS/DVB (50/30m)	2,5g	(Fish juice agar inoculated with different bacteria)	15 min at 40°C	40°C	30	GC-MS
12	HS-SPME	PDMS/DVB (65µm)	2,0g	Sample + 2mL water with NaCl (% different depending on species)	5 min	no mention	40	GC-MS
13 (C)	HS-SPME	CAR/PDMS/DVB (50/30m)	Whole fish (45± 3 g)	-	no mention	no mention	15	GC-FID + olfactometry
14 (D)	HS-SPME	CAR/DPMS/DVB (50/30m)	20g	Miced fish muscle	15 min at 40°C	40	30	GC-MS
15	HS-SPME	CAR/DPMS/DVB (50/30m)	5g	(fish oil)	10 min at 25°C	60	30	GC-MS
16	HS-SPME	PDMS (100µm)	Supernatant + 3g Na2SO4	2g muscle + 5mL water. Centrifuged (10 min, 4°C, 1500G)	10 min at 50°C, 250 rpm	50	20	GC-MS
17	HS-SPME	CAR/PDMS (75µm)	8g	Reduced to powder	30 min at RT	60	90	GC-MS
18	HS-SPME	CAR/PDMS/DVB	5g	(fish oil)	10 min at 25°C	60	30	GC-MS
19 (E)	HS-SPME + electric nose	PDMS/DVB	1g	2-3mm cubes of fish muscle	no mention	40	30	GC-MS
20 (F)	HS-SPME + HS-MS	CAR/PDMS (75µm)	24g	1 cm cubes	30 min at RT	50	2h	GC-MS
21	HS-SPME + SPME-Arrow	CAR/PDMS (75µm)	1mL	(fish sauce)	5 min	50	90	GC-MS
22	HS-SPME + TVBN	CAR/PDMS/DVB (50/30m)	0,5mL	Filletted, homogenized with 0,5N HCl then centrifuged	15 min with stirring	25	5	GC-MS

(2700g, 10', 5°C).

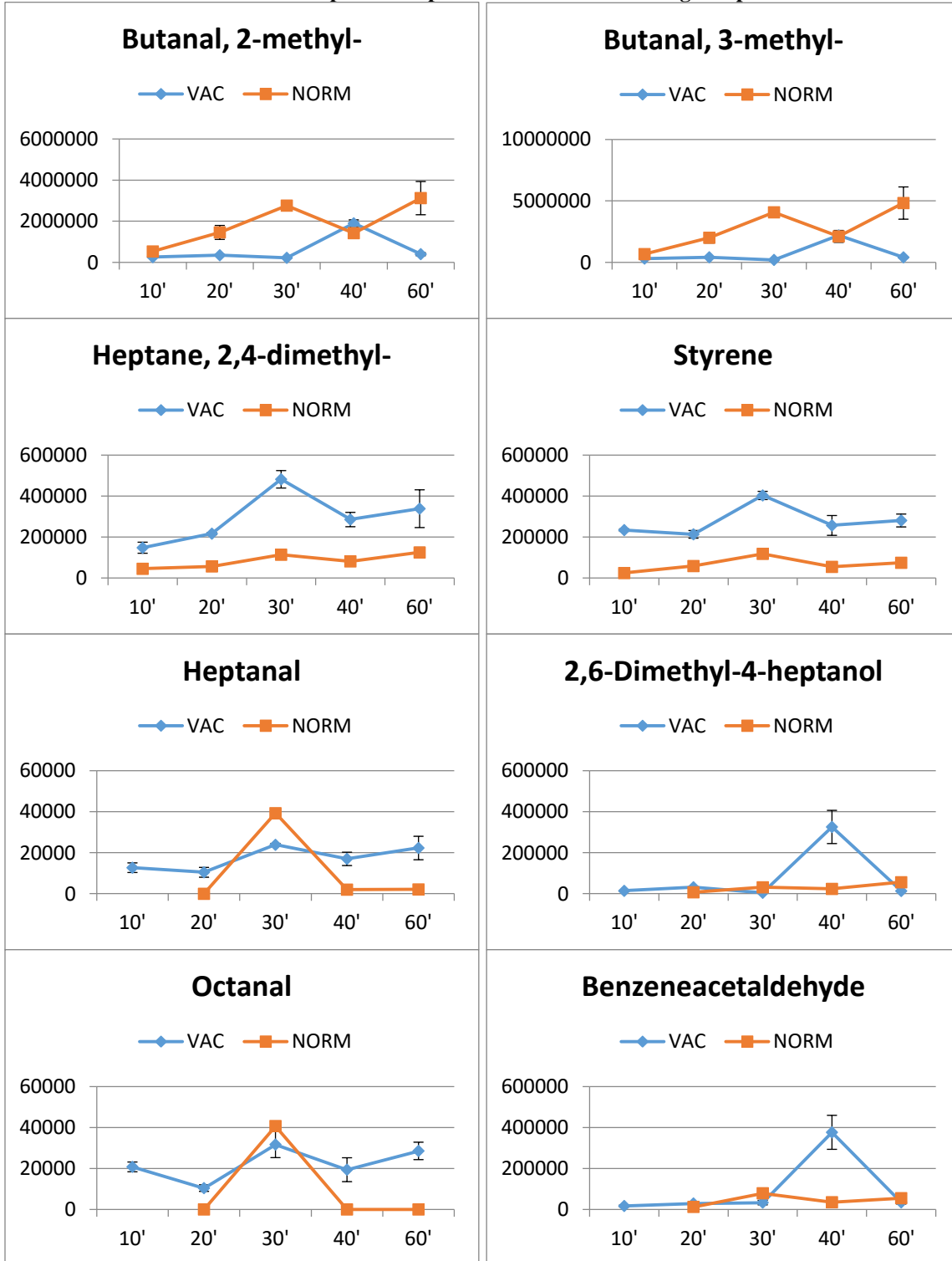
23 (G)	HS-SPME + TVBN	PDMS/DVB (65µm)	2g	Fillets	20 min at 50°C	50	30	GC-MS
24	MA-HS-SPME	CAR/PDMS (65µm)	5,0g	Sample + 10mL deionised water + 3g NaCl. pH 10. 80W, 5 min	no mention	no mention	5	GC-MS
25	Purge and trap concentrator	-	-	-	-	-	-	GC-MS
26	Purge and trap concentrator	-	-	-	-	-	-	GC-MS + olfactometry
27	SDE	-	-	-	-	-	-	GC-MS and GC-FID
28	SDE	-	-	-	-	-	-	GC-MS
29	Sensory	-	-	-	-	-	-	GC-MS
30	Sensory evaluation + SDE	-	-	-	-	-	-	GC-MS
31	TVBN	-	-	-	-	-	-	-
32	TVBN	-	-	-	-	-	-	-

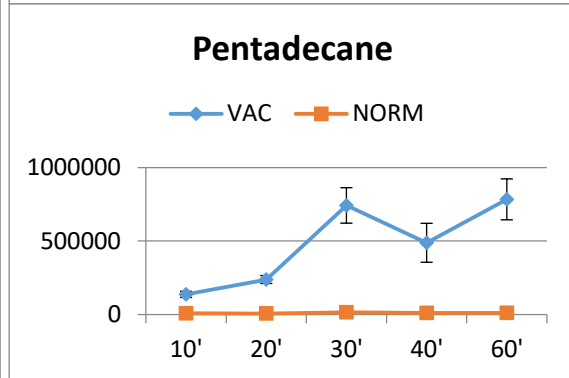
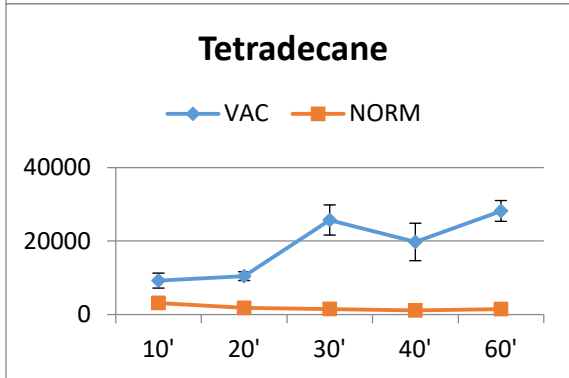
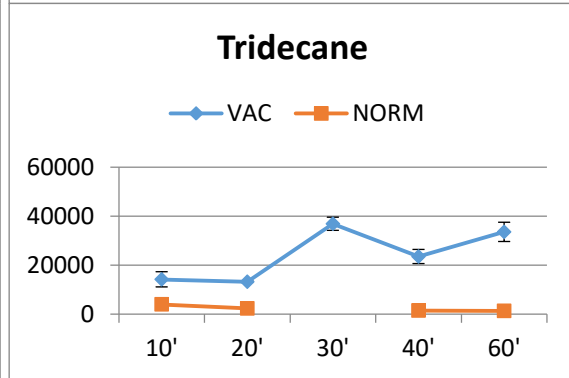
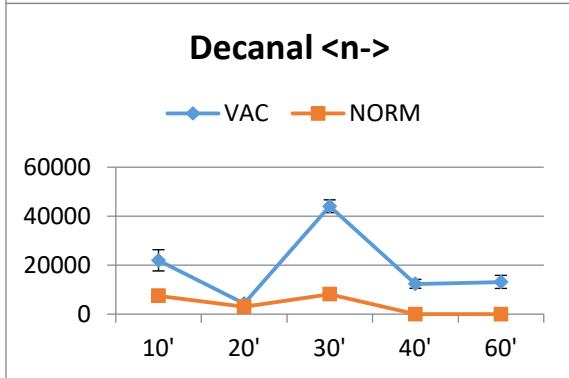
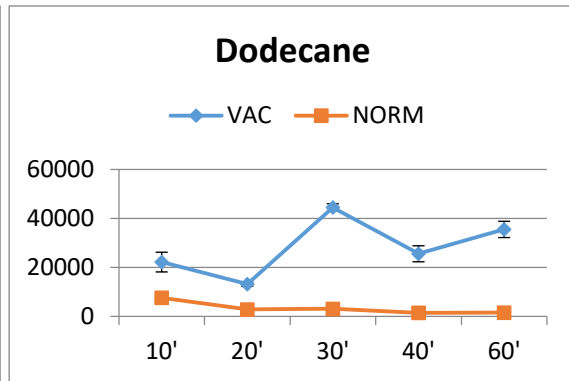
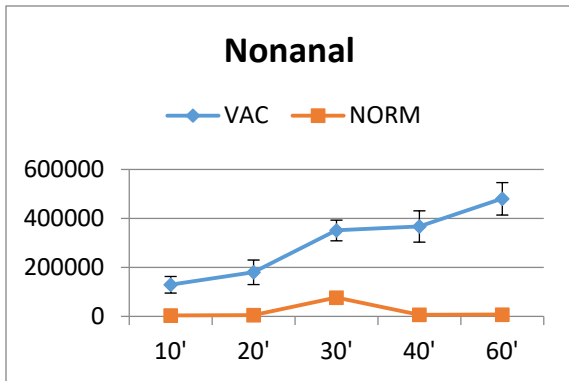
Annex 4 : raw fish volatiles compounds found in the literature

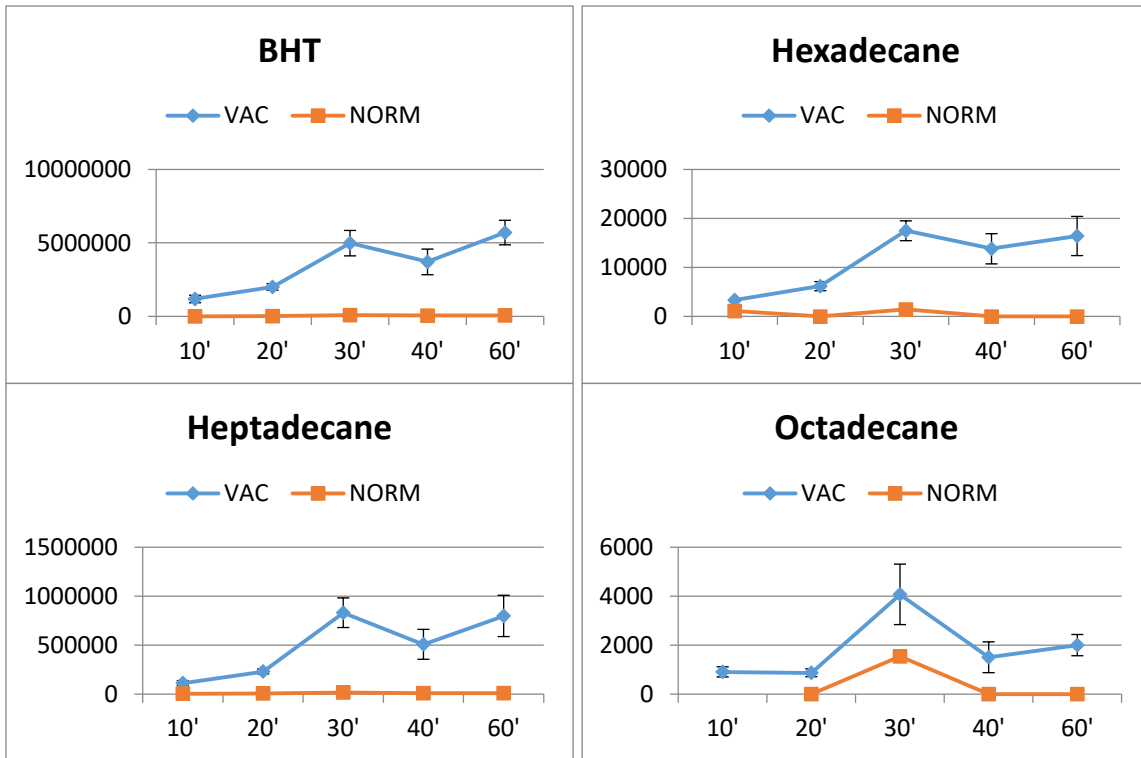
REF	Compound	REF	Compound	REF	Compound	REF	Compound
A, B, D, E, F, G	1-Hexanol	D, F	2-Penten-1-ol	D	1-Butoxy-2-propanol	A	3-Pentanone
A, B, D, E, F, G	1-Pentanol	B, D	2-Pentylfuran	G	1-Dodecanol	D	3-Phenyl-2-propenal
A, B, D, E, F, G	Hexanal	A, G	3,5,5-Trimethyl-2-hexene	B	1-Nonadecene	B	3-Undecanone
A, B, D, E, F, G	Nonanal	A, F	3-Methylbutanal	B	1-Nonanol	A	4,4-Dimethyl-1,3-dioxane
A, B, C, D, E	(E,E)-2,4-Heptadienal	A, F	3-Methyl-1-Butanol	C	1-octen-3-one	B	4-ethyl-Benzaldehyde
A, B, D, E, G	1-Heptanol	B, E	4-Heptenal	A	1-Penten-3-one	G	4-Hydroxybutyl acrylate
A, B, D, E, G	1-Octen-3-ol	B, E	5-Methyl-1,3,6-Heptatriene	F	1-Propanol	B	6-methyl-3-Heptanone
A, B, D, E, F	2-Ethyl-1-Hexanol	D, F	Acetone	G	2-(2-ethoxyethoxy)-Ethanol	B	6-methyl-5-Hepten-2-one
A, B, D, E, G	Heptanal	D, F	Decane	D	2,2,4,6,6-Pentamethylheptane	E	6-nonadienal
A, B, D, E, G	Octanal	A, F	Dimethyl sulfide	F	2,3-Butanediol	B	8-Heptadecene
A, B, D, G	1-Octanol	A, F	Ethanol	A	2,4-Heptadienal	F	Acetic acid
A, B, D, E	1-Penten-3-ol	A, D	Ethyl acetate	E	2,4-Hexadienal	A	Acetic acid, ethyl ester
A, B, D, E	2,3-Octanedione	B, D	Heptadecane	D	2,5-Hexandione	G	Acetoin
A, B, D, E	2,3-Pentanedione	B, D	Hexadecane	G	2,5-Octanedione	F	Acetonitrile
B, D, E, G	2-Octen-1-ol	D, F	Hexane	D	2,6-Nonadienal	D	Acetophenone
A, B, E, G	3,5-Octadien-2-one	A, F	Methanethiol	A	2-Butanol	A	Cyclohexanone
A, D, F, G	Benzaldehyde	B, G	Naphthalene	A	2-Butanone	D	Dichlorometane
B, D, E, F	Dodecane	D, F	Nonane	B	2-Decanone	F	Dimethyl disulfide
A, B, D, E	Pentanal	D, F	Octane	A	2-Ethyl furan	F	Dimethyl trisulfide
B, D, E, F	Tridecane	A, F	Pentane	B	2-ethyl-1,4-dimethyl-Benzene	B	Dodecanal
A, C, E, F	Trimethylamine	A, D	Propanal	B	2-ethyl-Furan	D	E-2-heptenal
B, D, E, F	Undecane	E, G	Undecanal	B	2-Heptanone	D	E-2-hexenal
A, C, E	(E)-2-Hexenal	D, F	Xylene	A	2-Hexanone	D	E-2-octenal
B, C, E	(E,Z)-2,6-Nonadienal	B	(E)-2-Heptenal	B	2-Hexenal	D	E-2-pentenal
A, B, E	(Z)-2-Penten-1-ol	B	(E)-2-Hexen-1-ol	A	2-Methyl butanal	D	Ethylbenzene

D, E, F	2-Ethylfuran	B	(E)-2-Nonenal	A	2-Methyl-1-butanol	B	Hexadecanal
A, D, F	3-Hydroxy-2-Butanone	B	(E)-2-Octen-1-ol	F	2-Methylbutanal	G	Hexanoic acid
A, D, F	Acetaldehyde	B	(E)-2-Penten-1-ol	D	2-nonen-1-ol	C	methional
A, B, E	Butanal	A	(E)-2-Pental	F	2-Nonenal	A	Methylene chloride
A, D, F	Carbon disulfide	C	(E,E)-2,4-decadienal	B	2-Undecenal	B	N,N-dimethyl- Methylamine
A, D, F	Heptane	B	(E,E)-2,4-Hexadienal	B	3,5,5-trimethyl-1-Hexene	B	Nonadecane
A, E, F	Limonene	C	(E,E)-2,4-nonadienal	D	3,5-Octadien-3-ol	G	Nonanoic acid
B, D, E	Pentadecane	C	(E,Z)-3,5-octadien-2-one	G	3,7-dimethyl-1,6-Octadien-3-ol	G	Octanoic acid
B, D, E	Tetradecane	B	(S)-1-methyl-4-(1-methylethenyl)-Cyclohexene	G	3-Cyclohexene-1-ethanol	F	Phenylethyl alcohol
B, D, F	Toluene	C	(Z)-1,5-octadien-3-one	A	3-Heptanone	D	Propylbenzene
B, E	Decanal	F	(Z)-2-Hexen-1-ol acetate	D	3-Hexanone	D	Styrene
B, E	(E)-2-Octenal	A	(Z)-4-Heptenal	C	3-methylnonane-2,4-dione	B	Tetradecanal
C, E	(E,Z)-2,4 decadienal	B	(Z,Z)-1,4-Cyclooctadiene	D	3-Methylpentane	D	Tetrahydrofuran
D, E	(E,Z)-2,4-Heptadienal	B	(Z,Z)-9,12-Octadecadien-1-ol	D	3-Octanone	C	trans-4,5-epoxy (E)-2-decenal
A, F	1-Butanol	G	1,2-Benzenedicarboxylic acid, bis (2-methylpropyl) ester	D	3-Octen-2-one	B	Tridecanal
A, F	2,3-Butanedione	G	1,4-Butanediol	A	3-Pentanol	D	Z-4-heptenal
A, F	2-Methyl-1-propanol	D	1,5-octadien-3-ol				

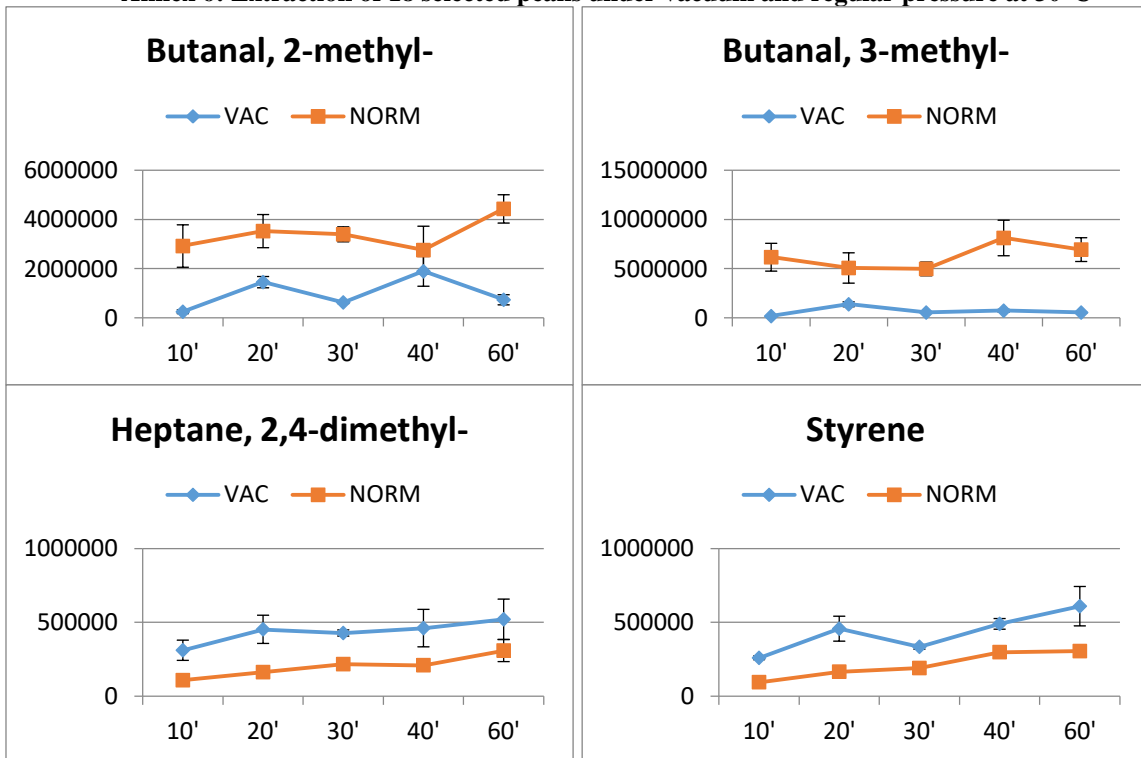
Annex 5: 18 selected peaks sampled under vacuum and regular pressure at 5°C

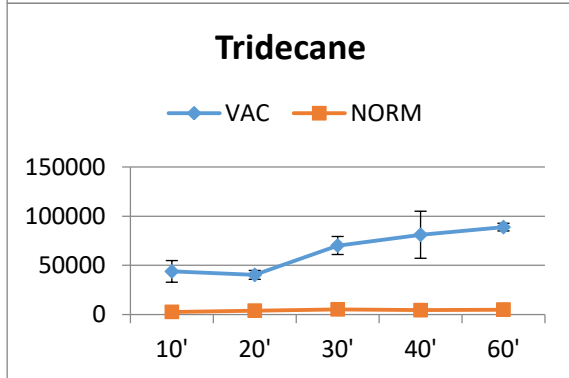
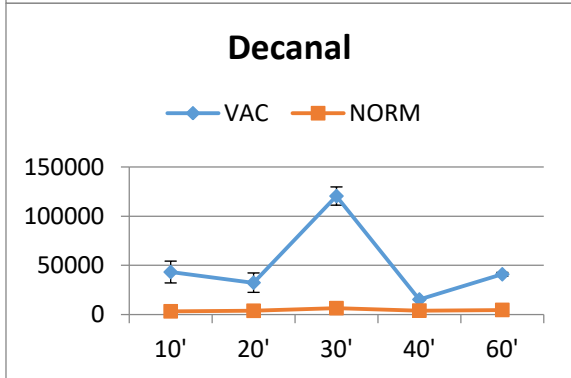
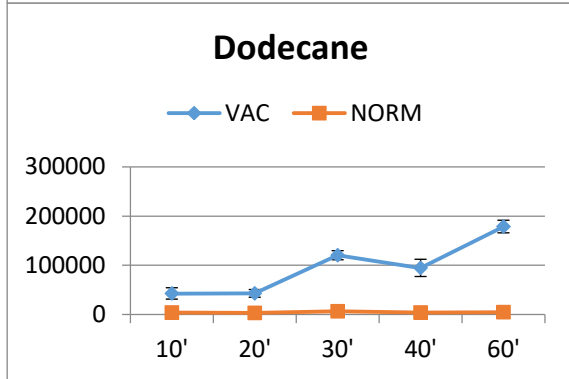
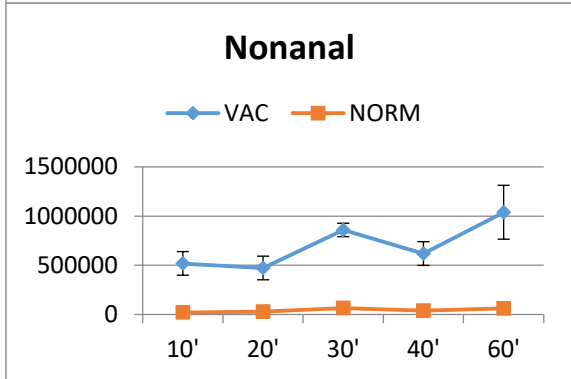
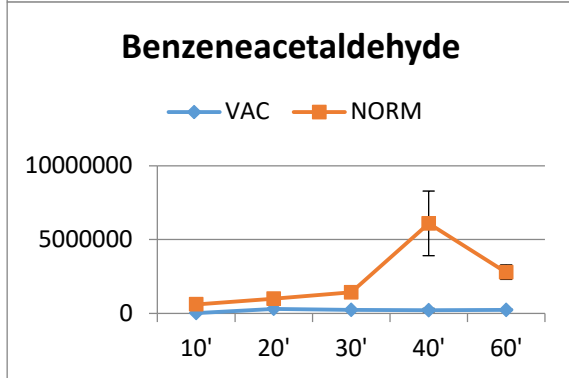
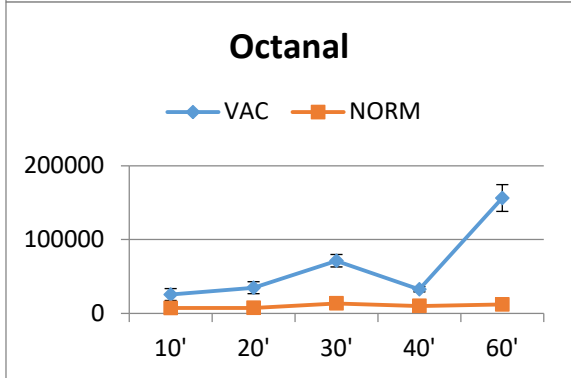
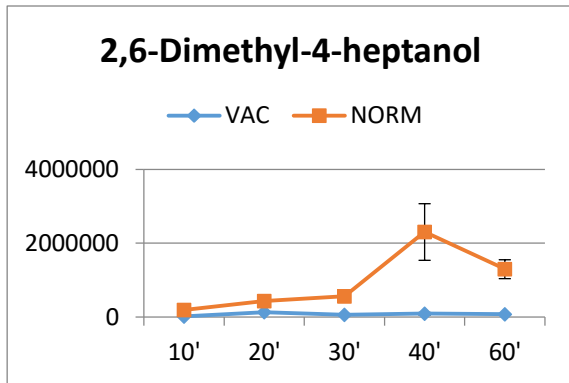
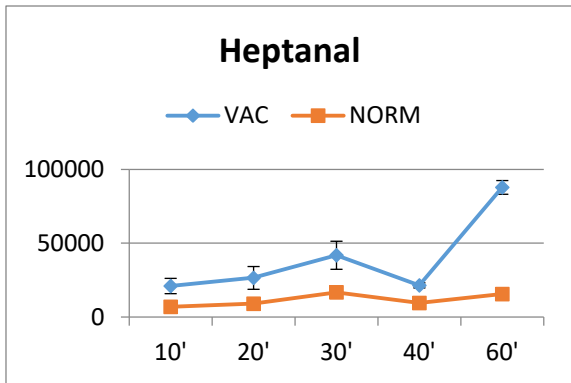


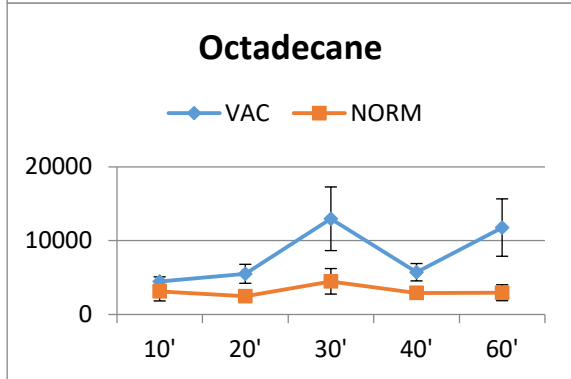
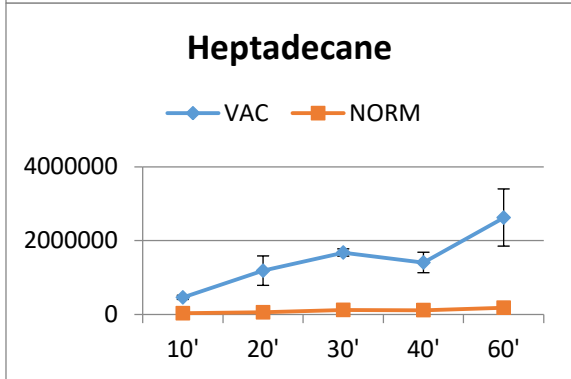
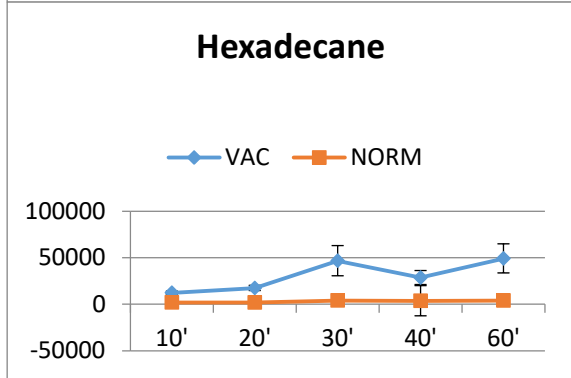
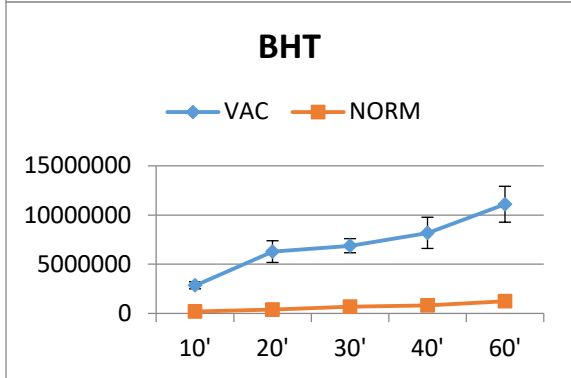
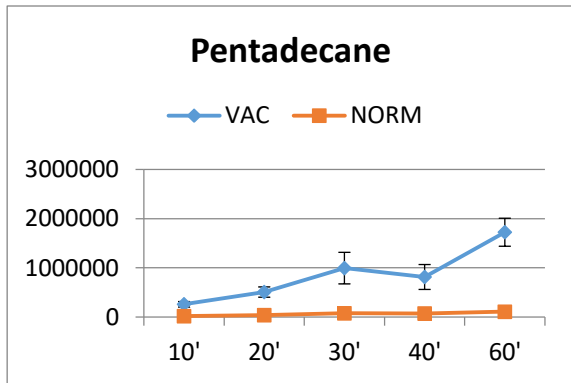
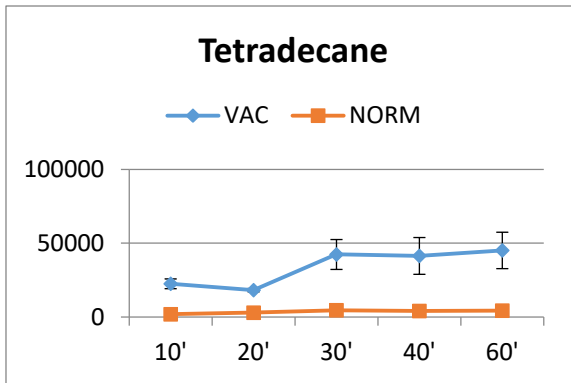




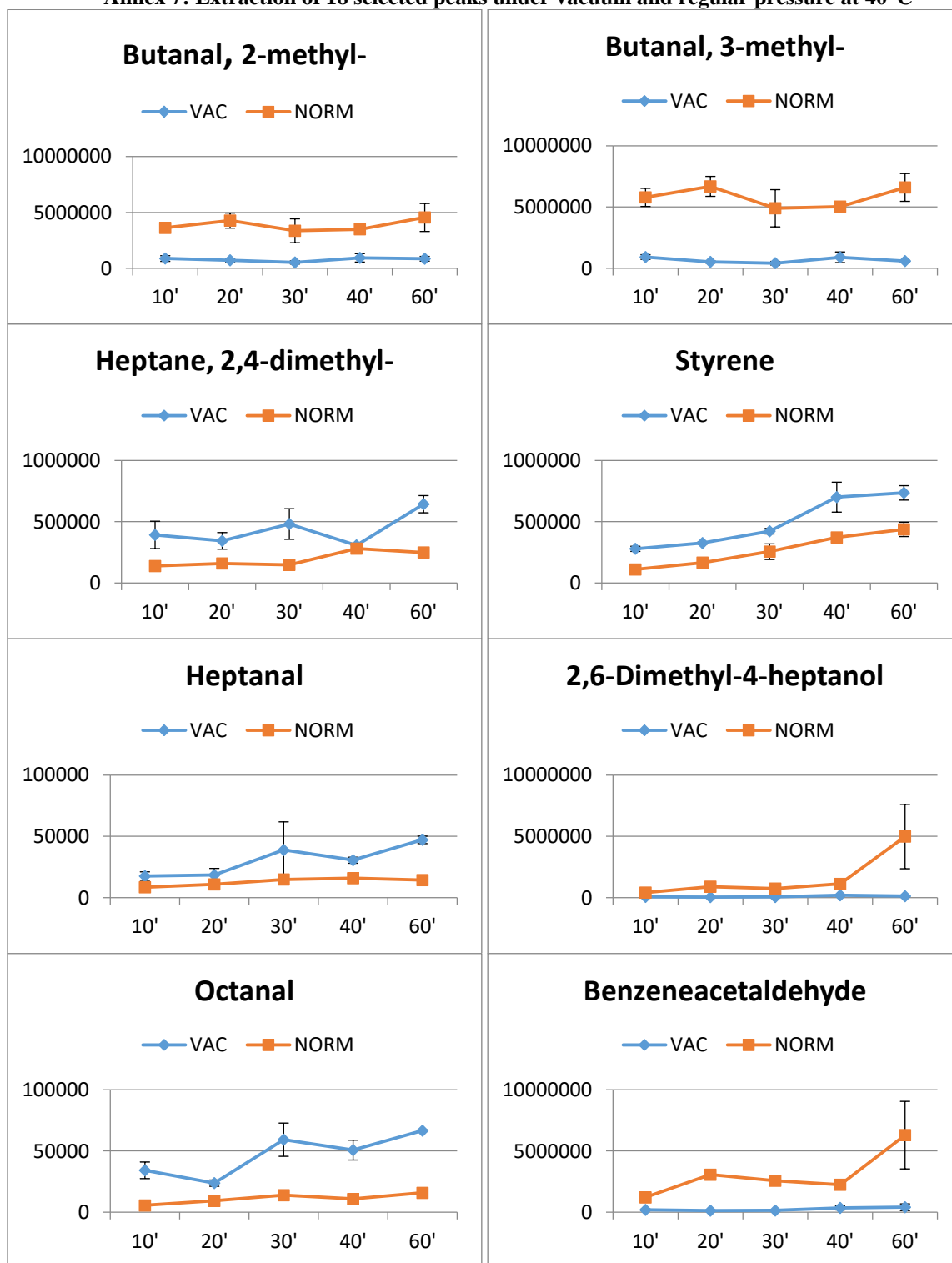
Annex 6: Extraction of 18 selected peaks under vacuum and regular pressure at 30°C

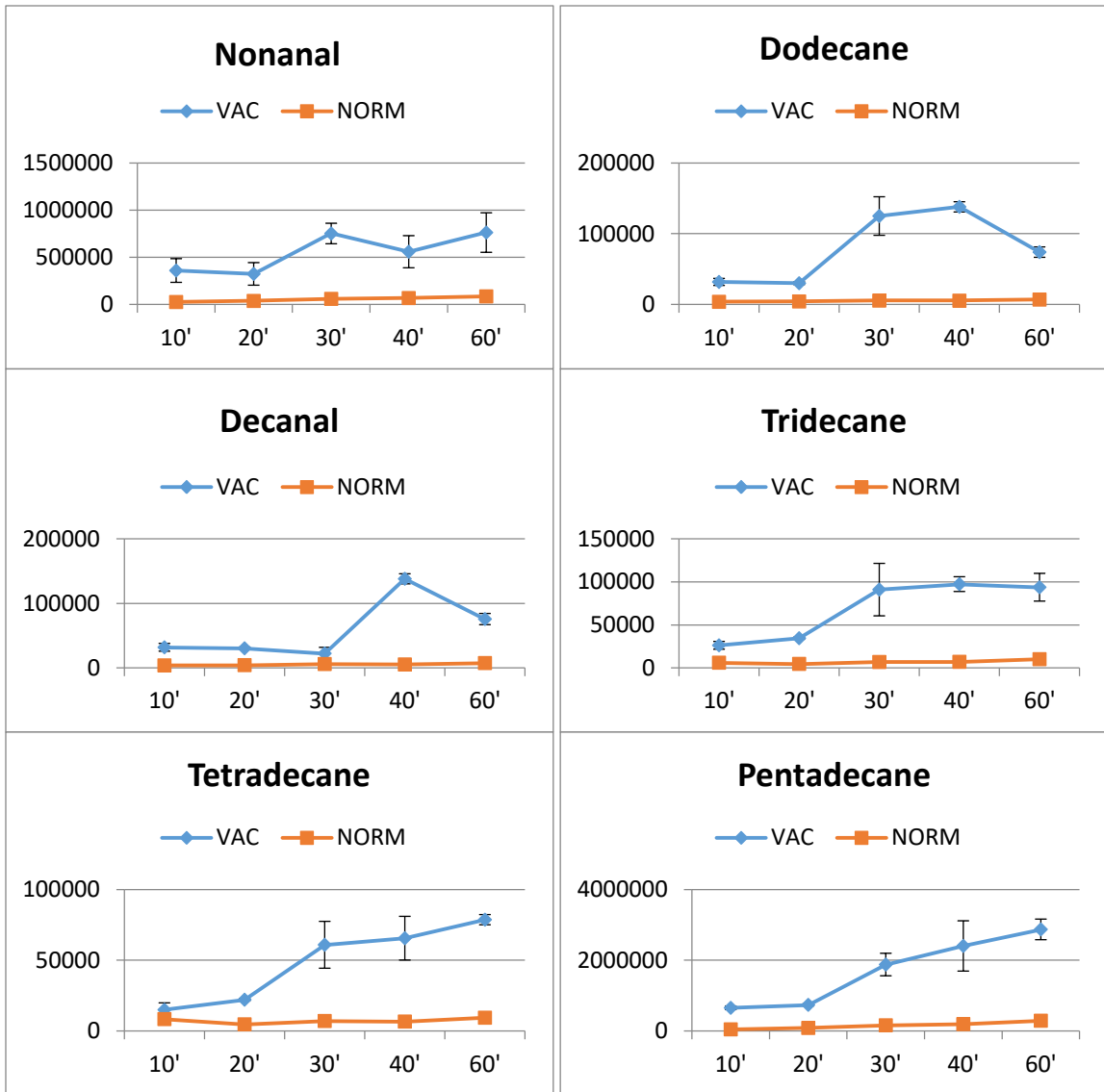


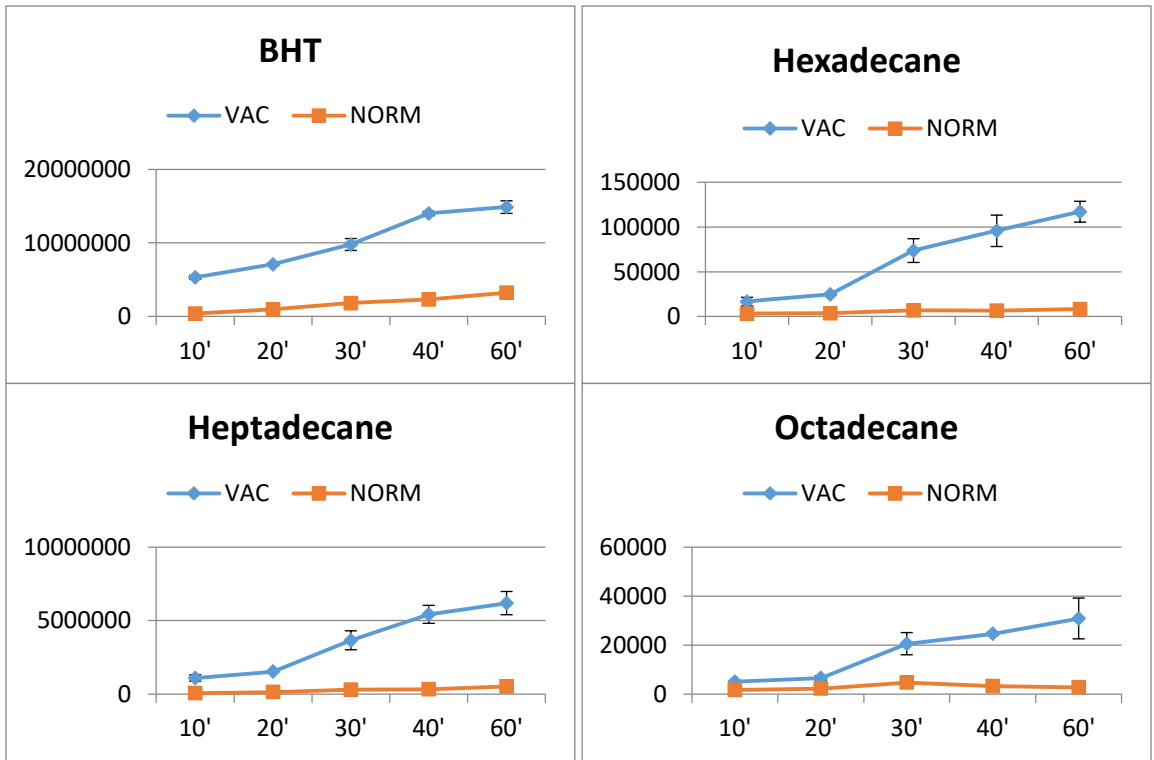




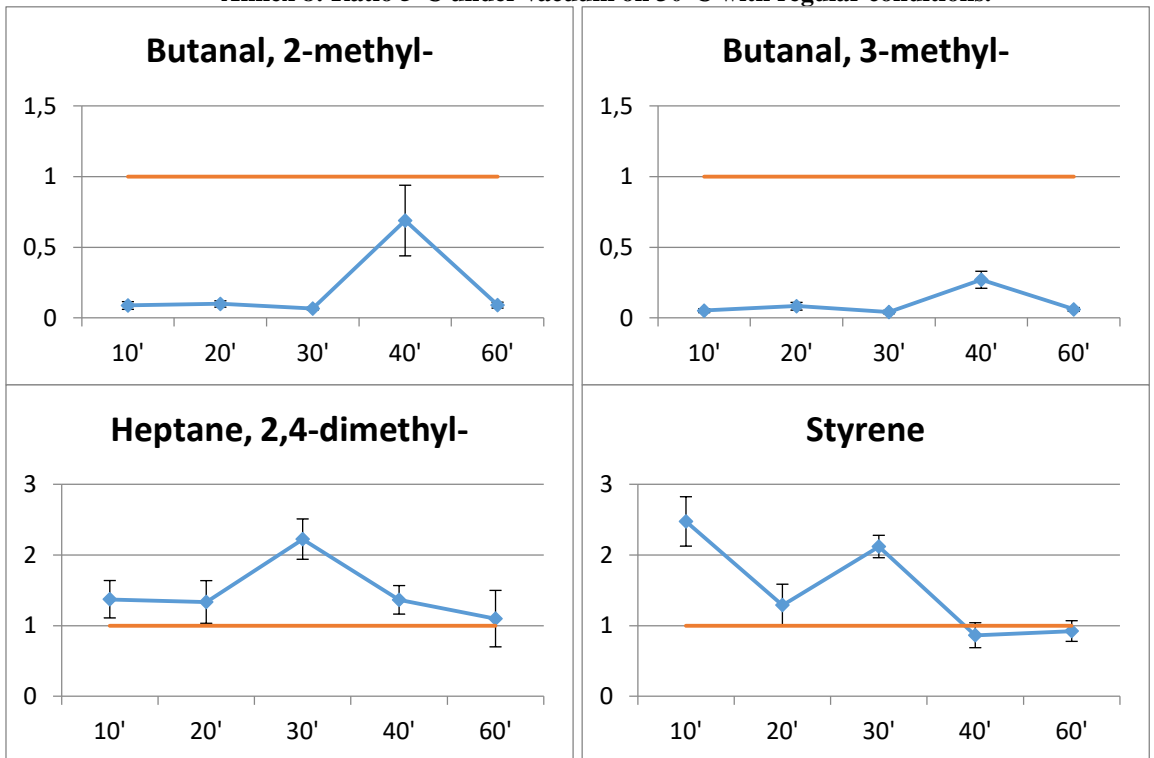
Annex 7: Extraction of 18 selected peaks under vacuum and regular pressure at 40°C

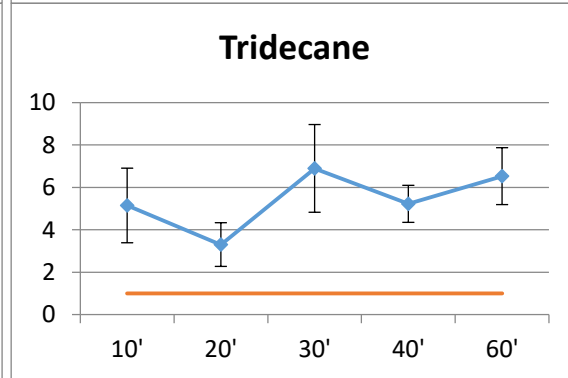
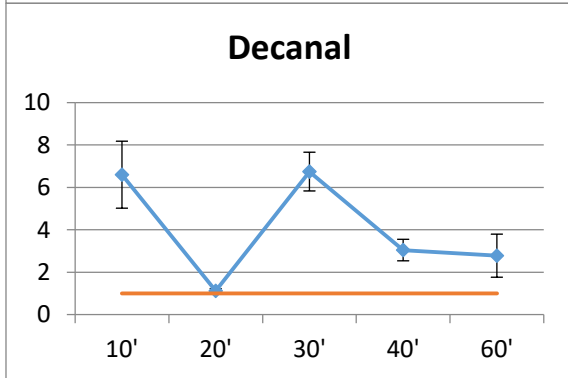
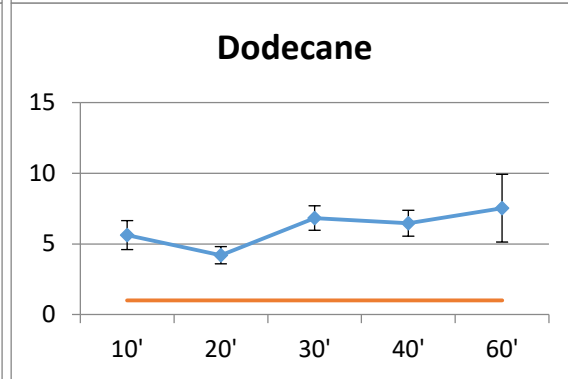
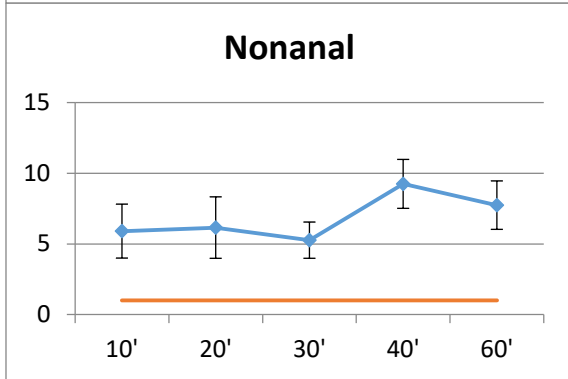
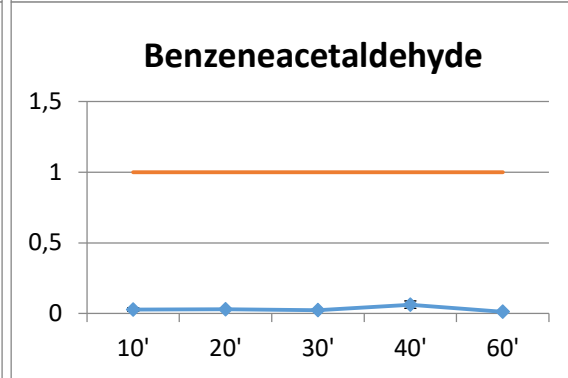
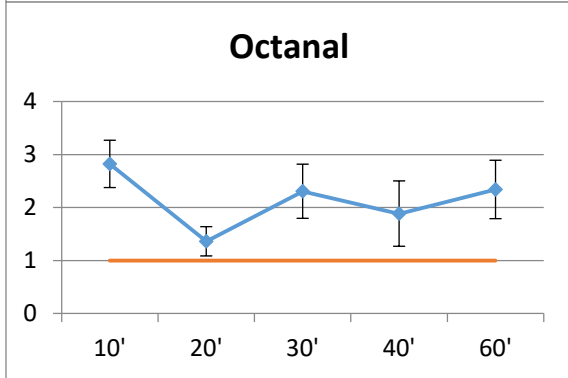
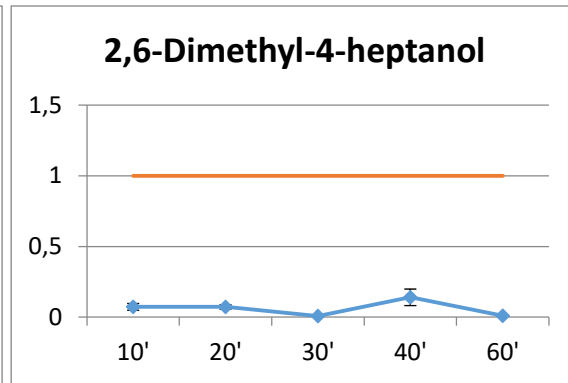
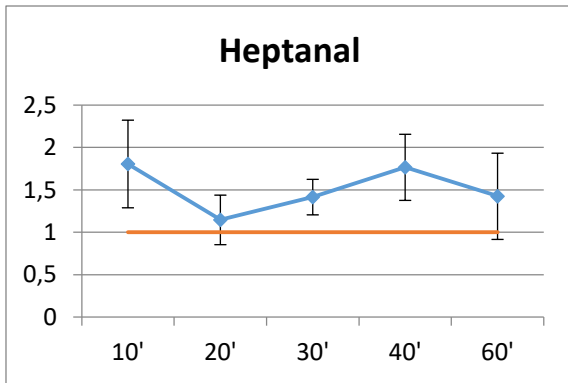


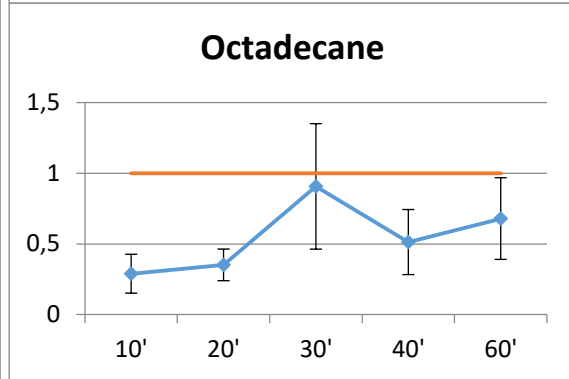
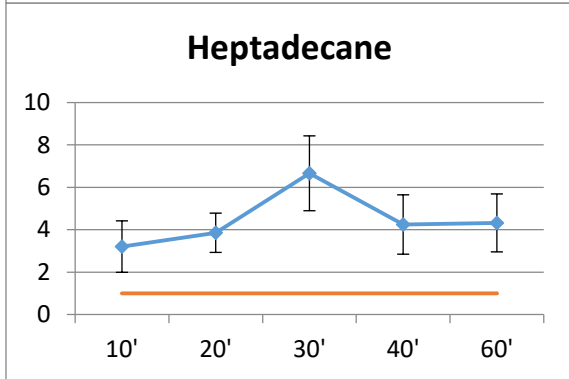
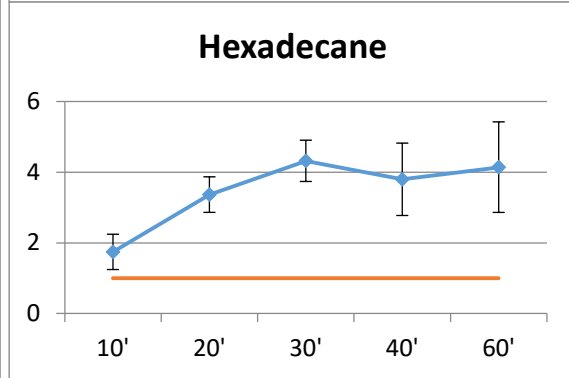
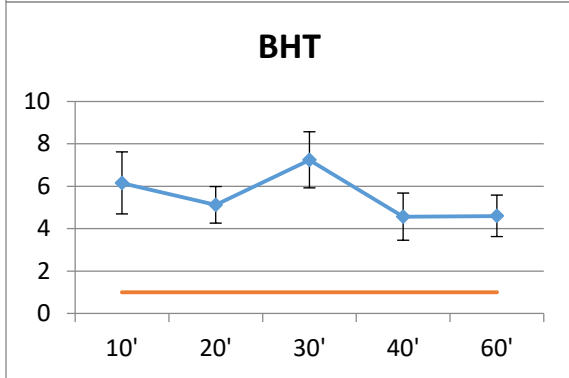
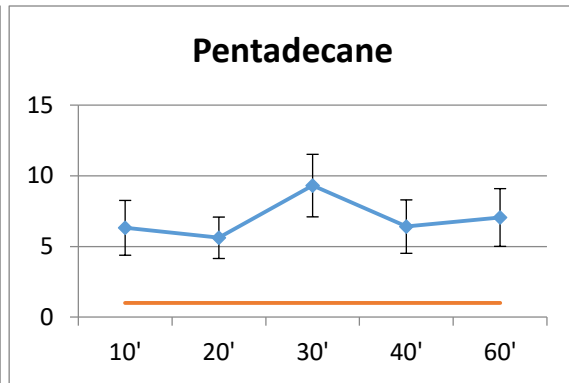
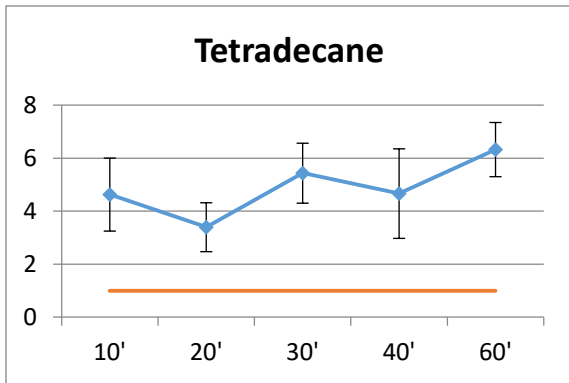




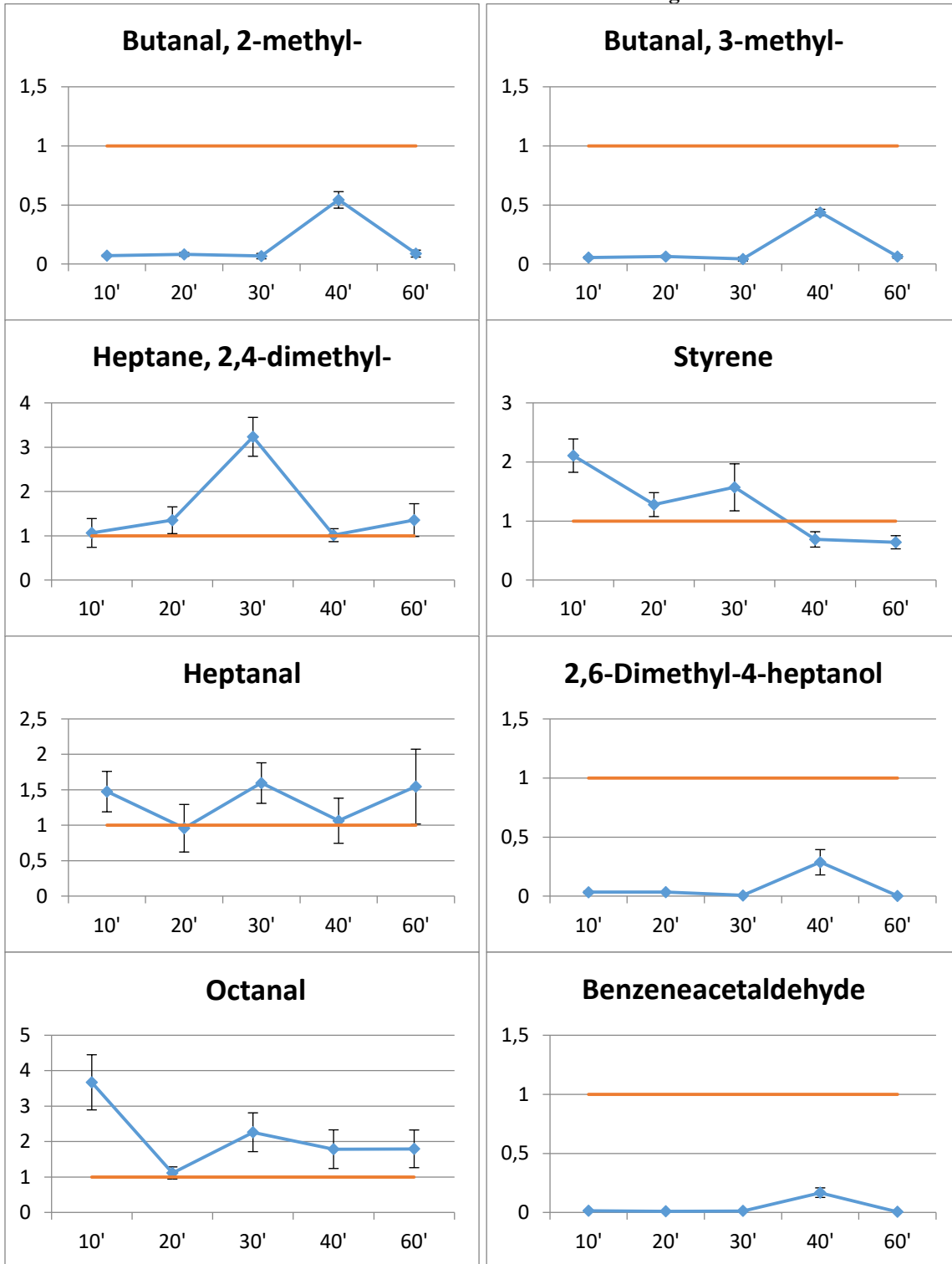
Annex 8: Ratio 5°C under vacuum on 30°C with regular conditions.

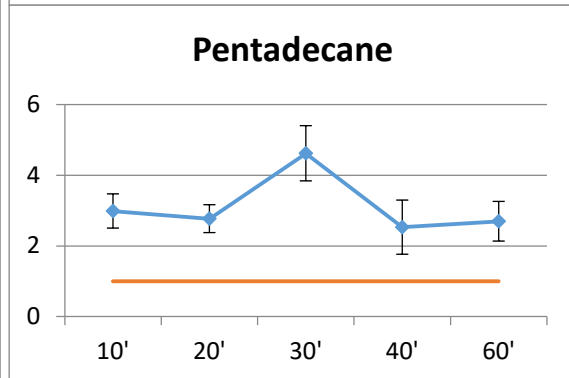
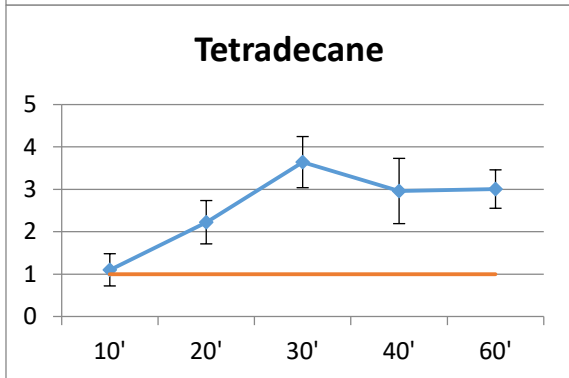
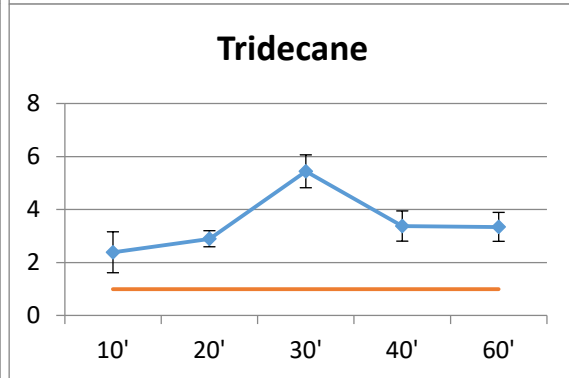
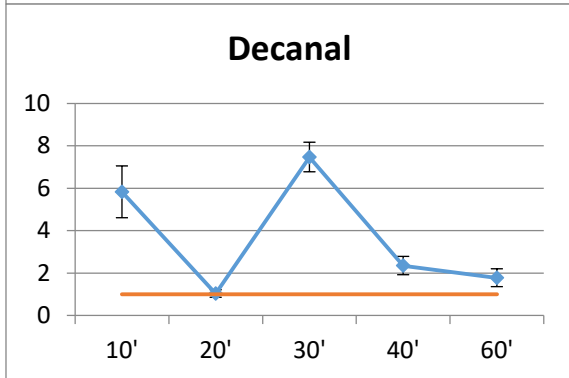
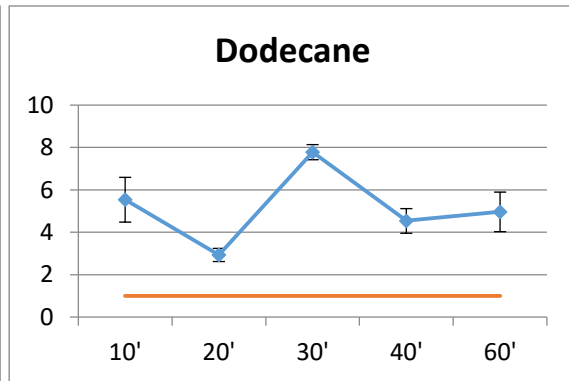
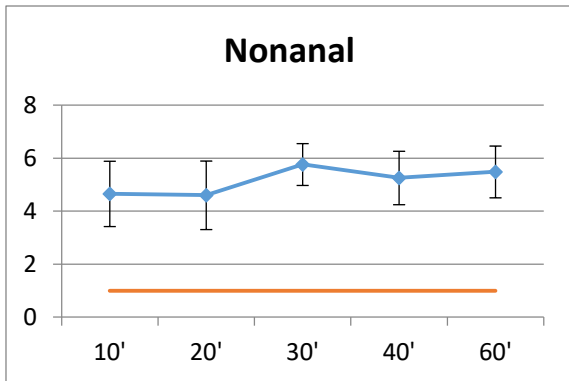


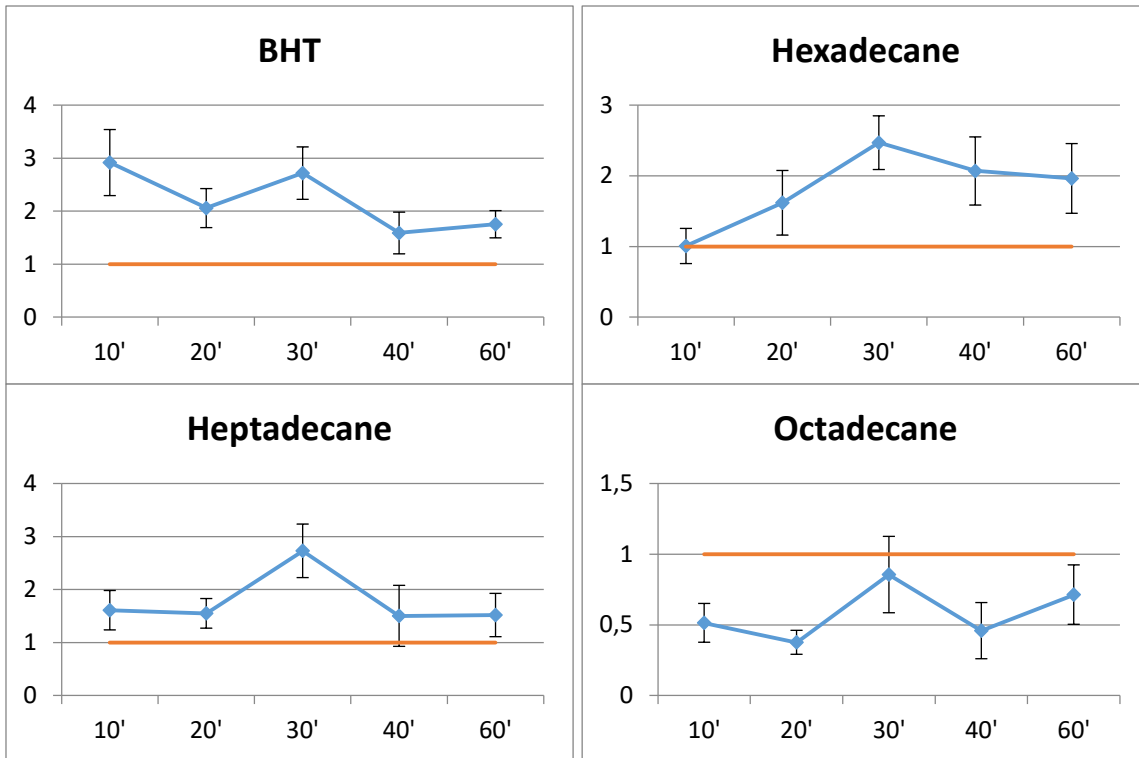




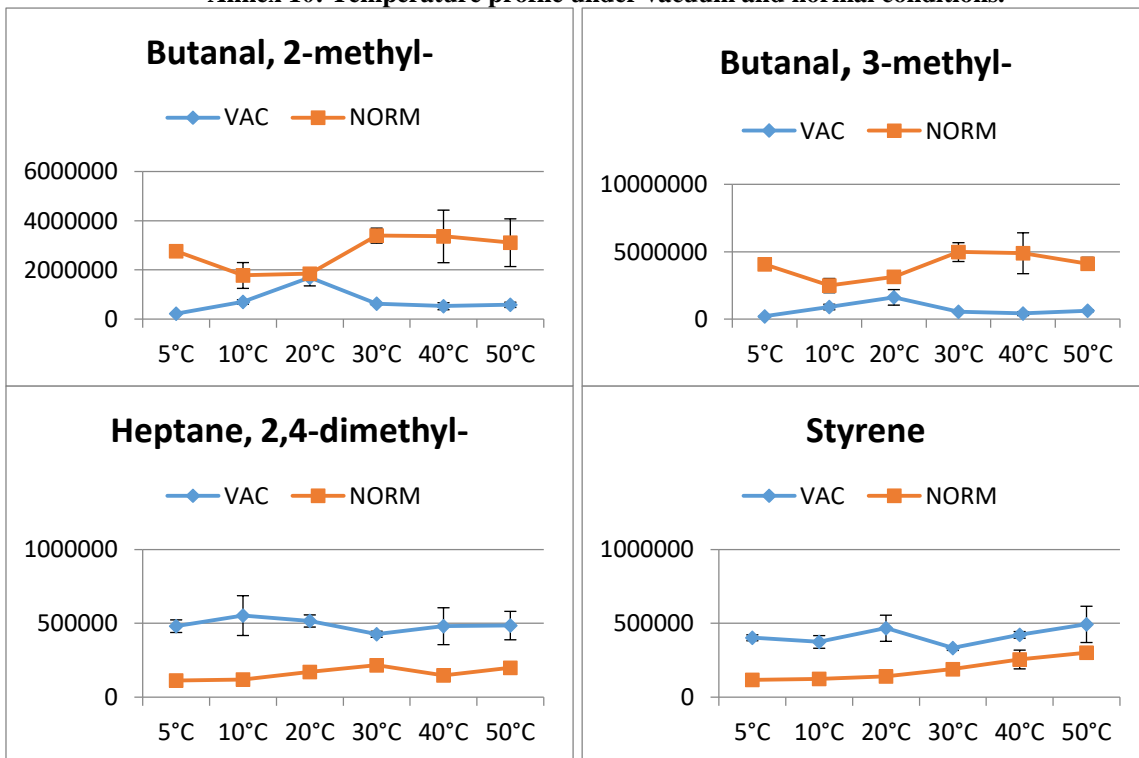
Annex 9: Ratio 5°C under vacuum on 40°C with regular conditions.

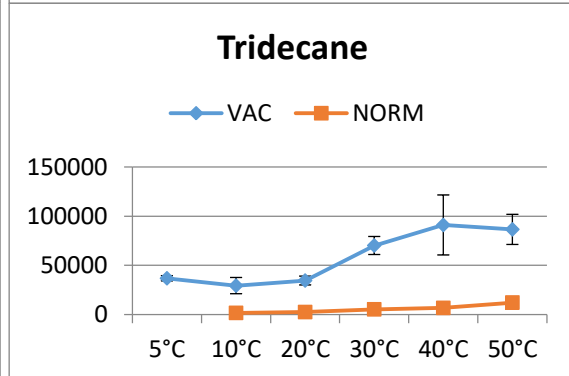
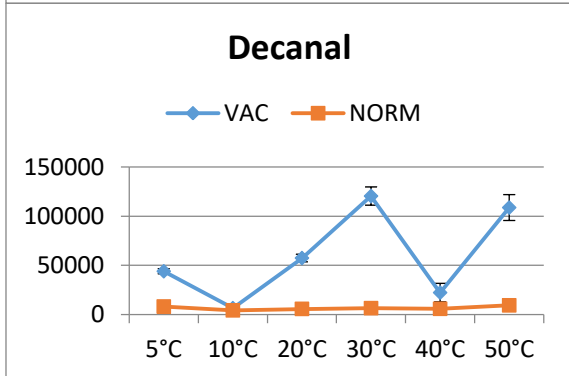
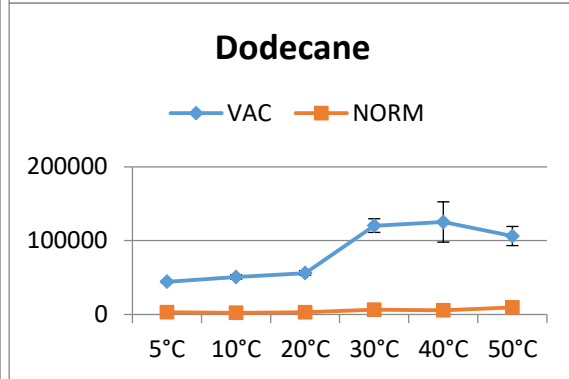
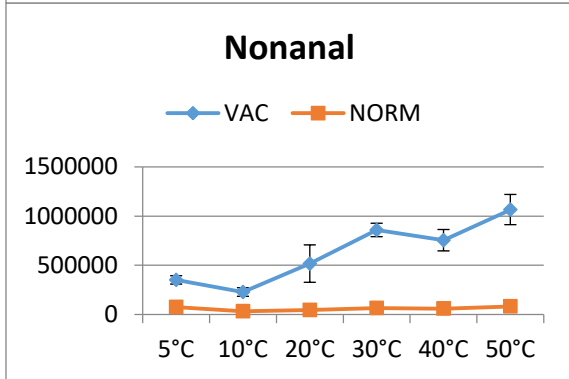
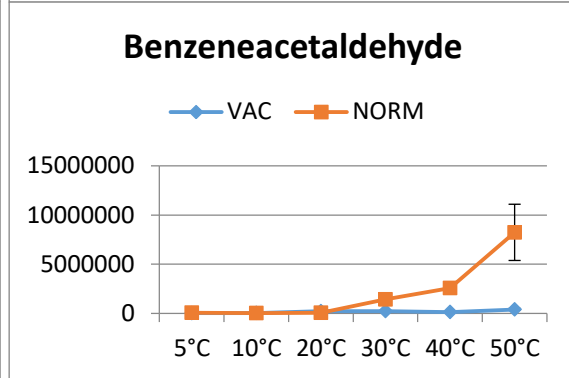
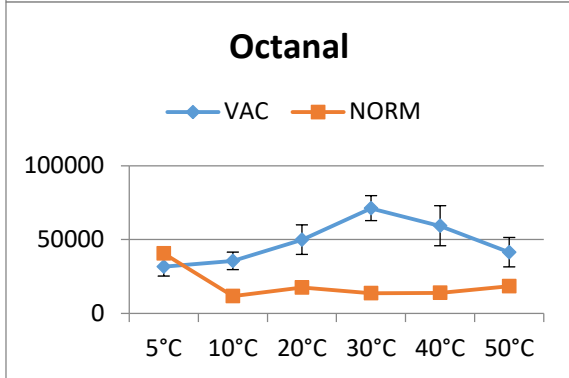
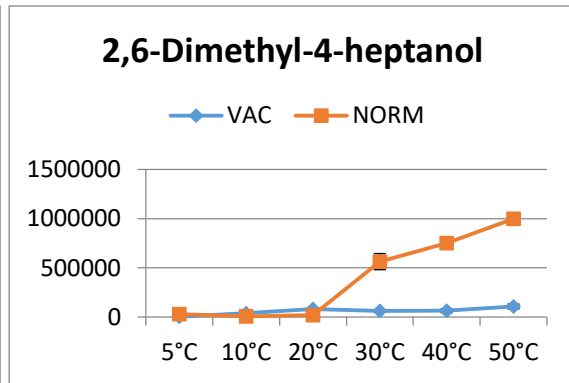
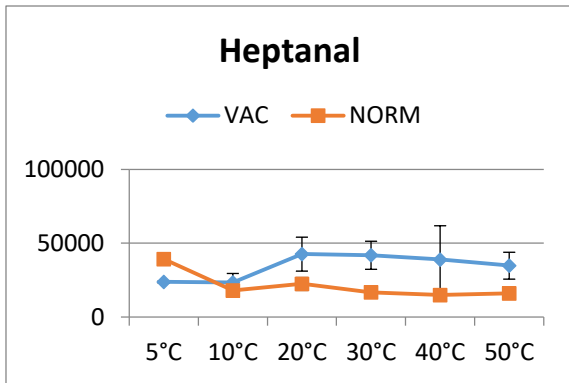


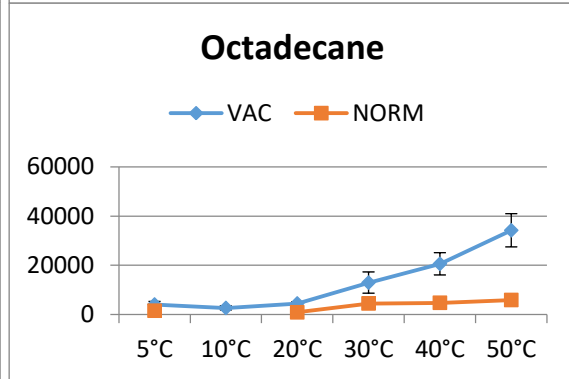
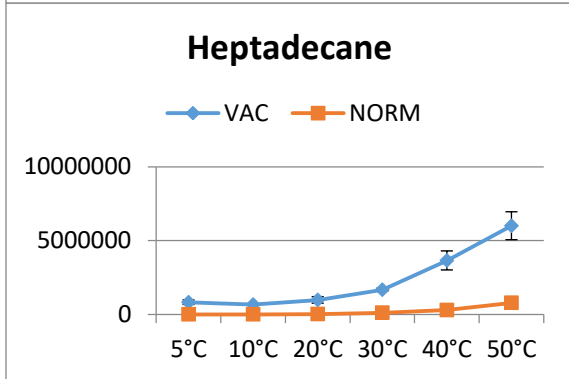
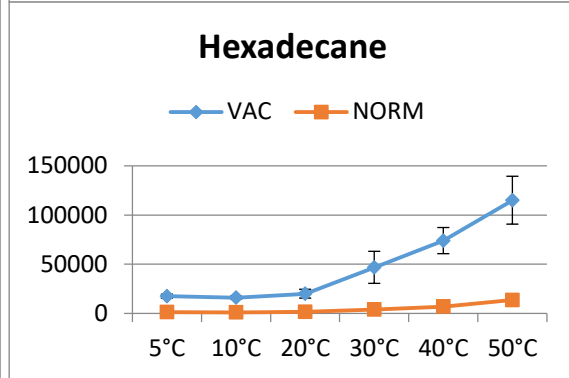
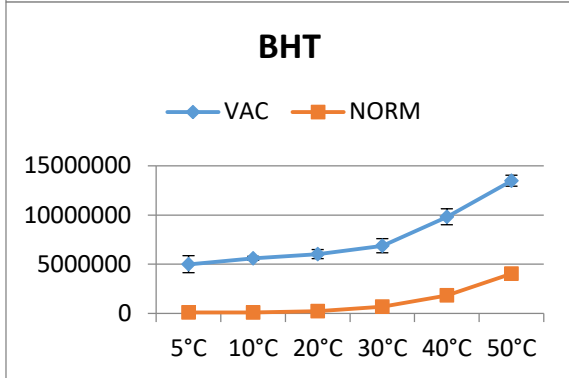
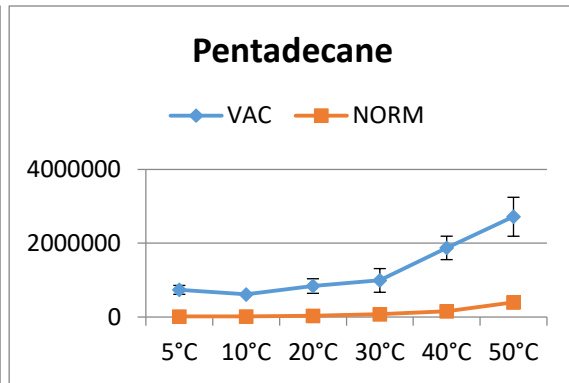
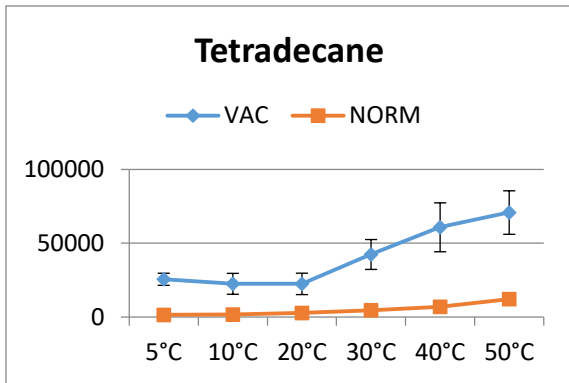




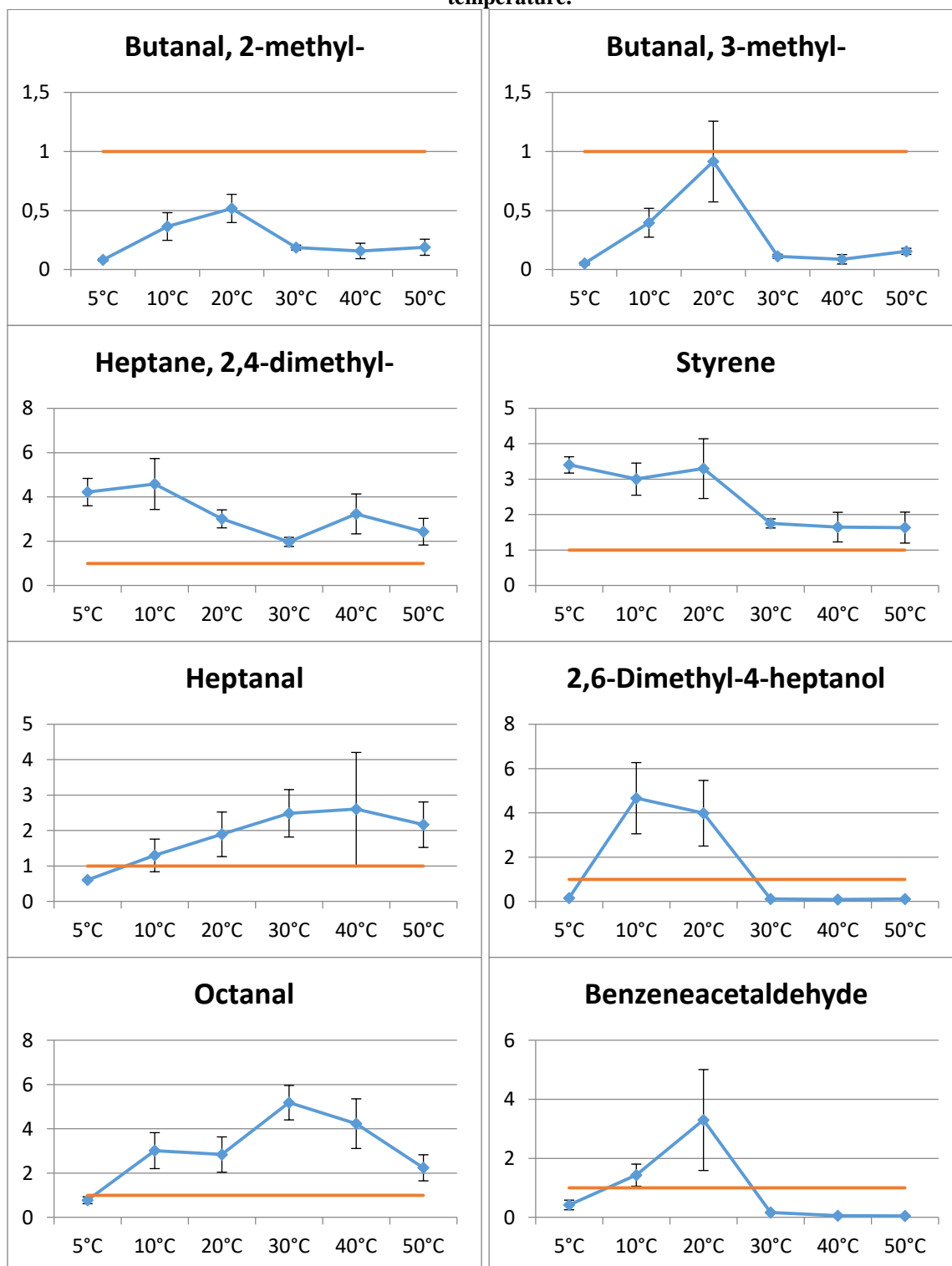
Annex 10: Temperature profile under vacuum and normal conditions.

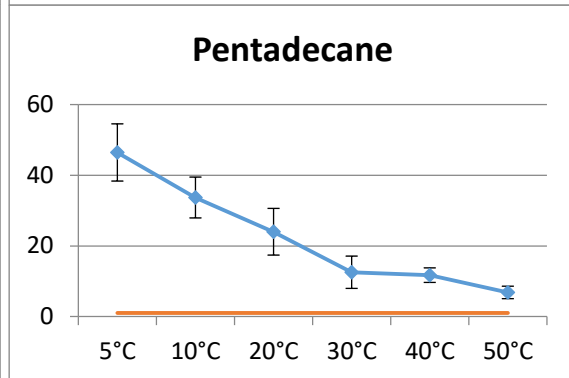
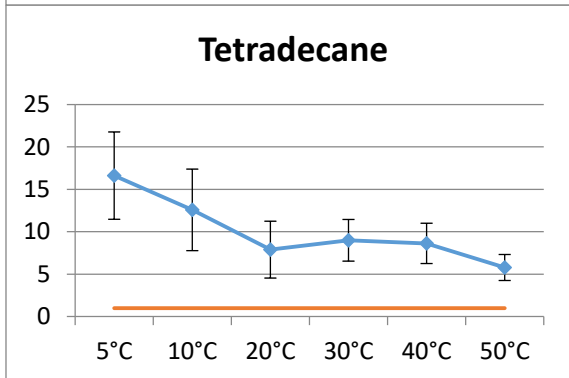
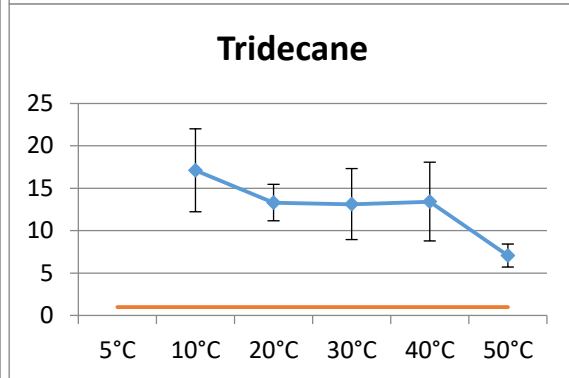
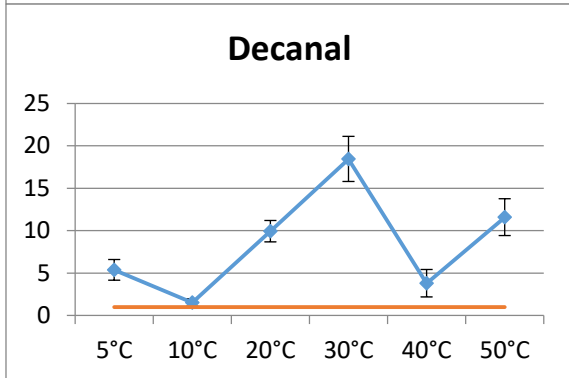
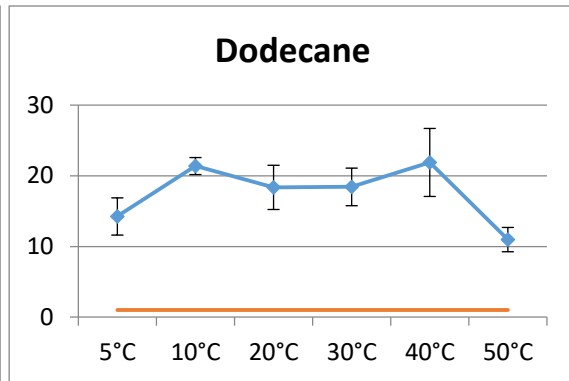
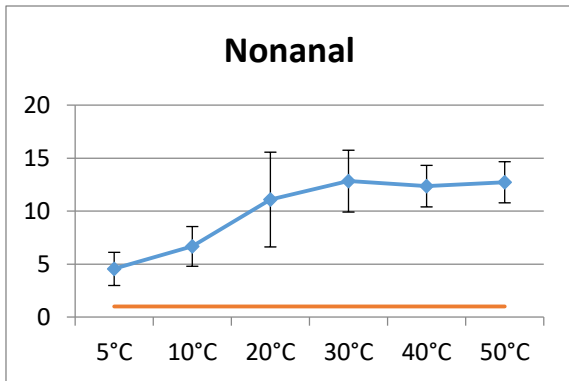


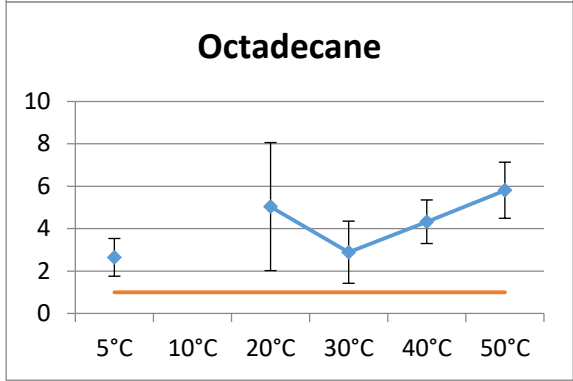
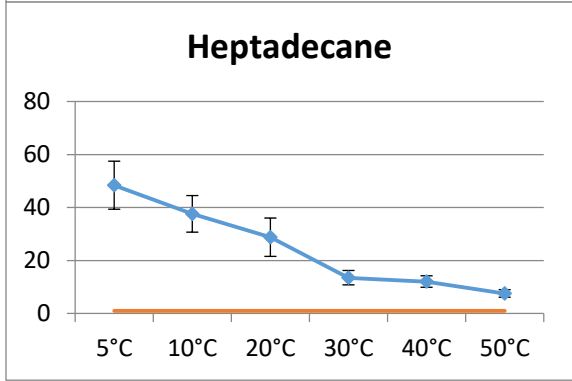
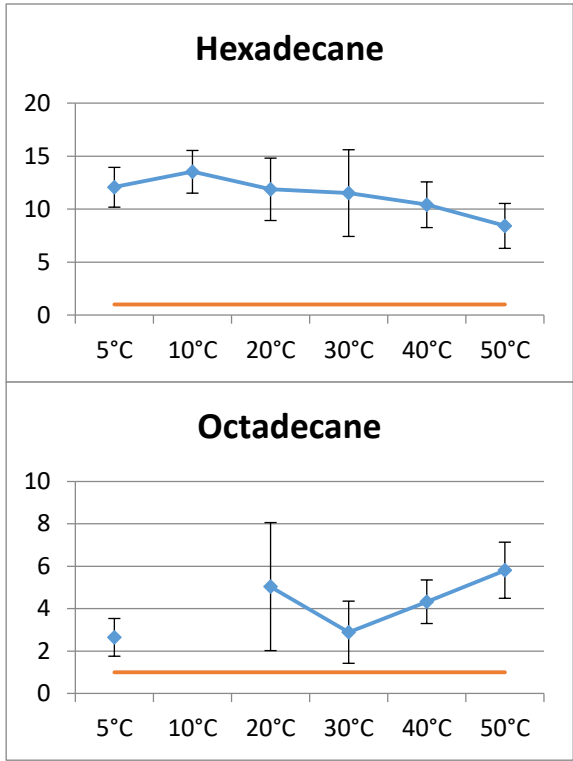
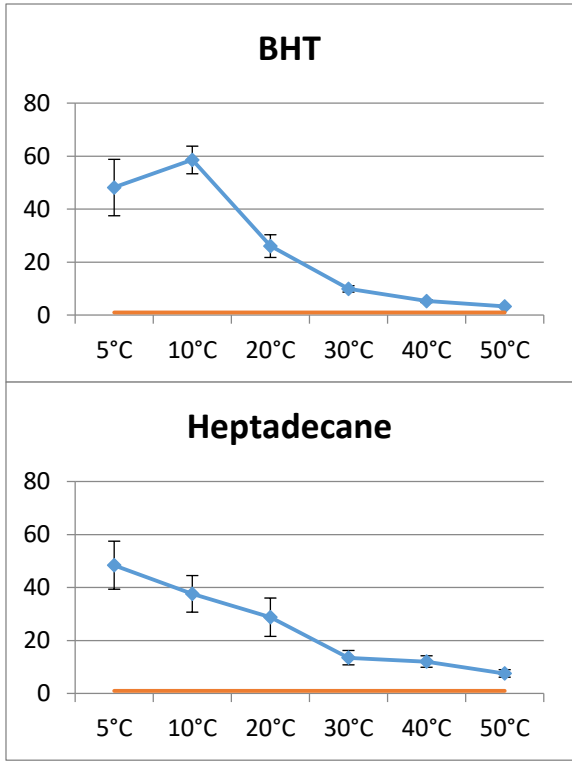




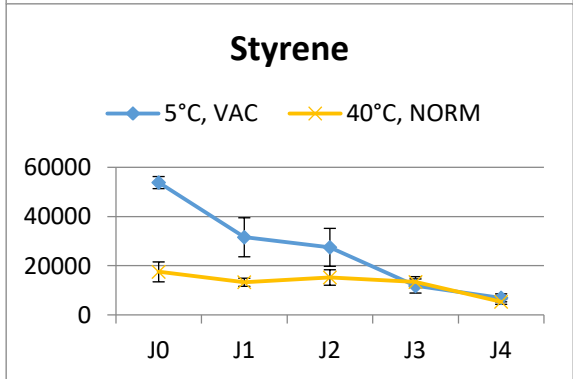
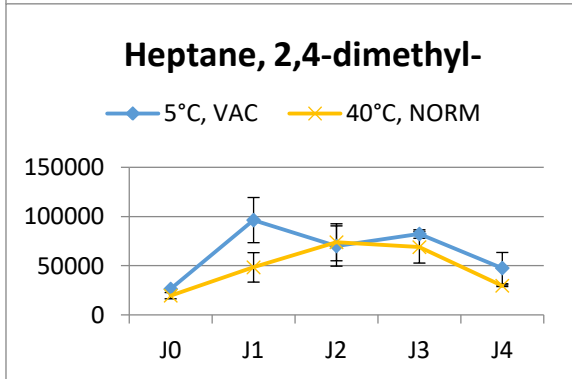
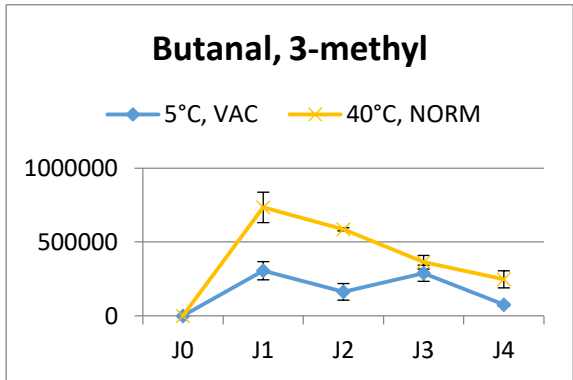
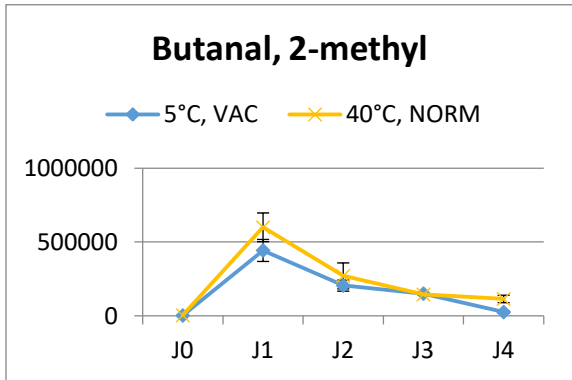
Annex 11: ratio of the extraction under vacuum on the extraction with normal conditions, with increasing temperature.

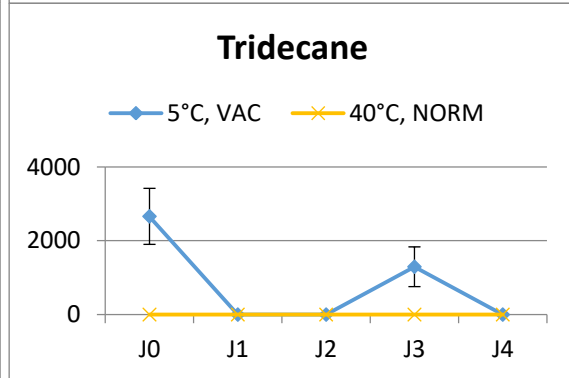
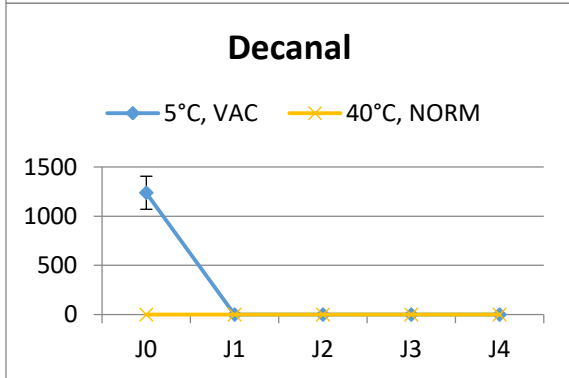
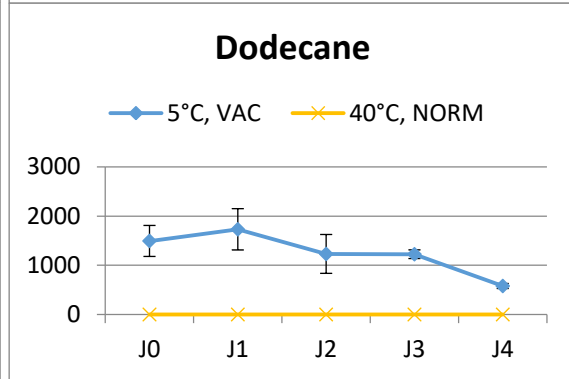
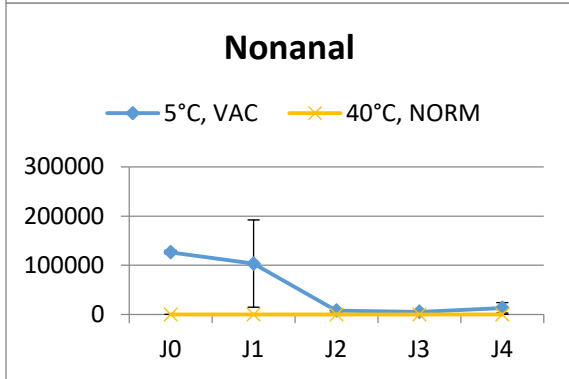
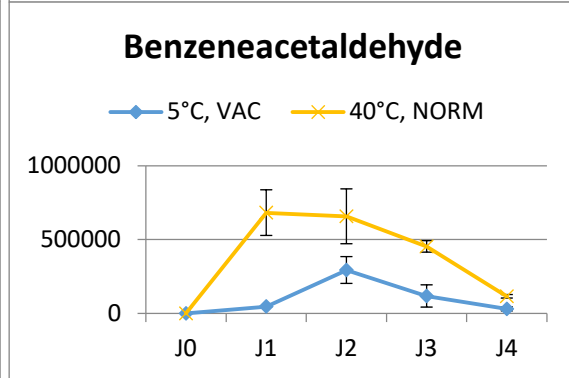
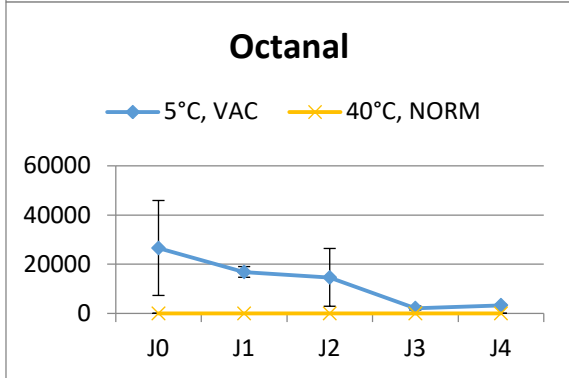
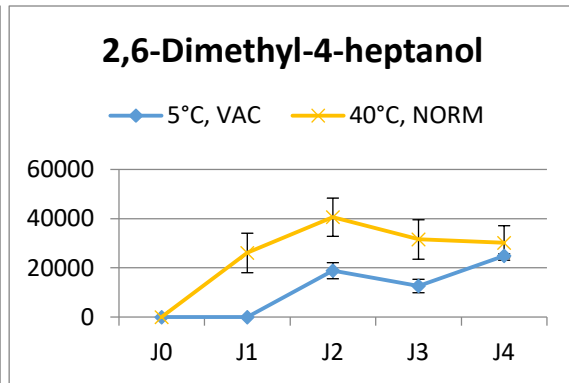
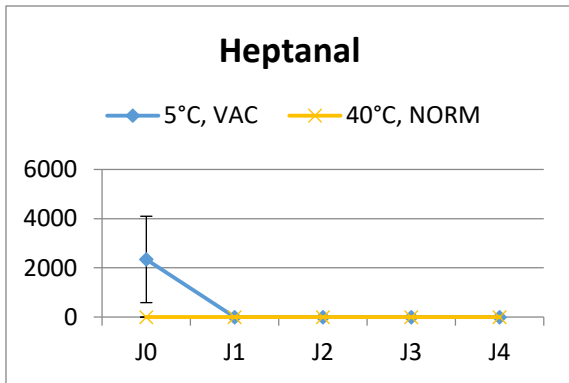


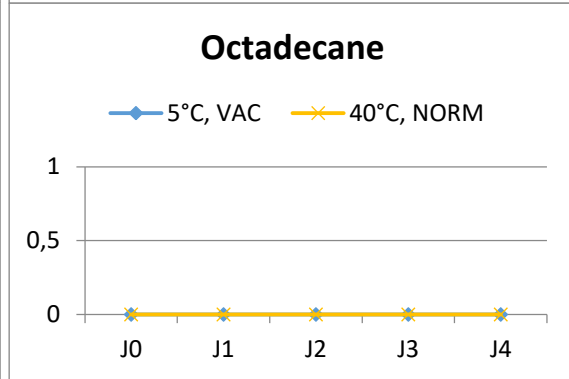
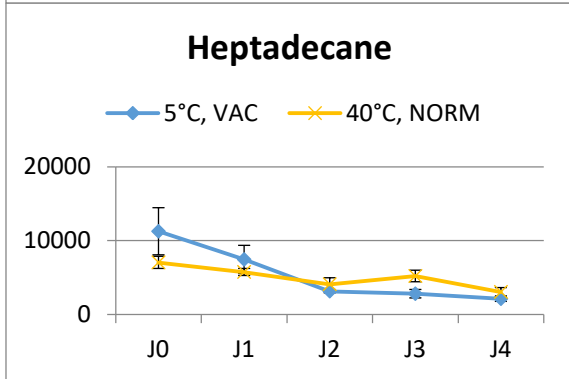
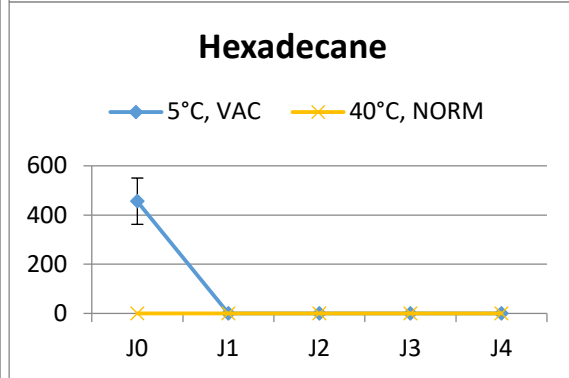
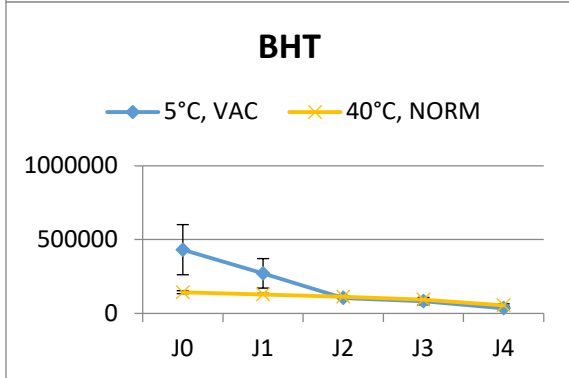
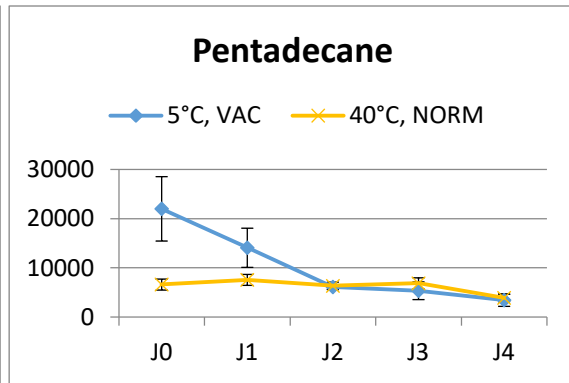
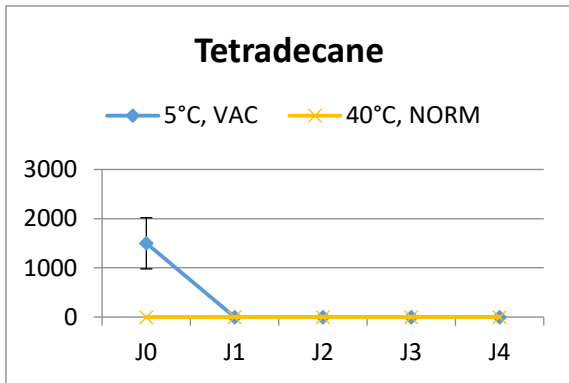




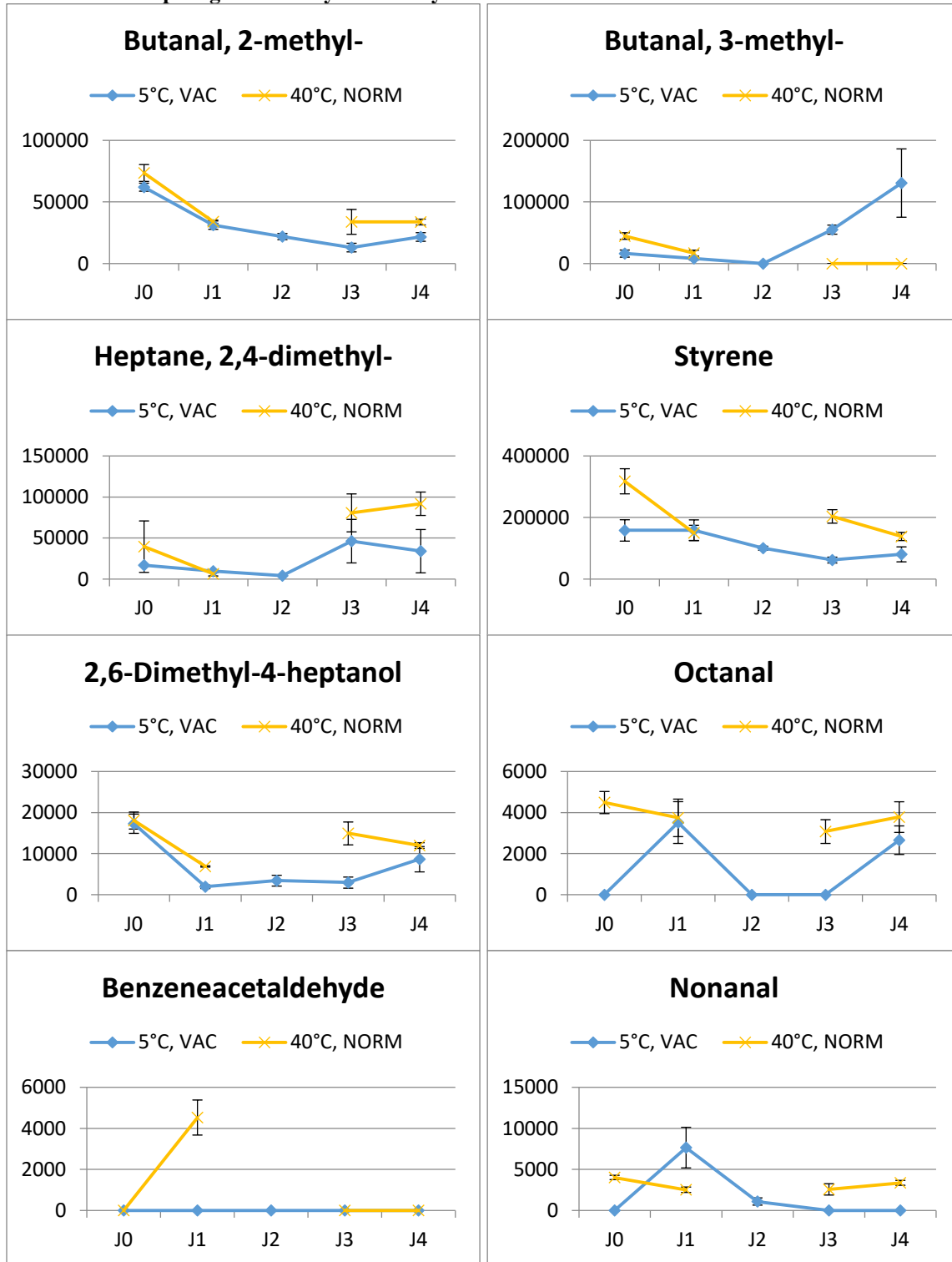
Annex 12: Salmon spoilage over 5 days and analyzed at 5°C under vacuum and 40°C with normal conditions.

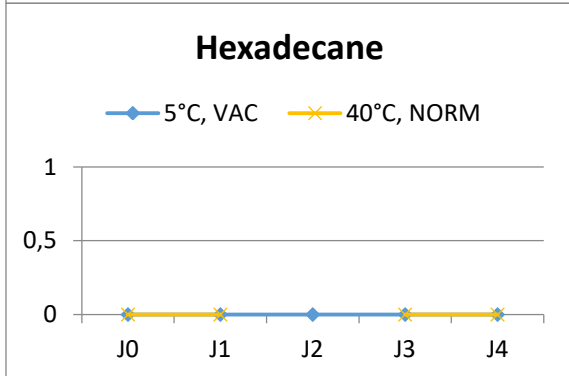
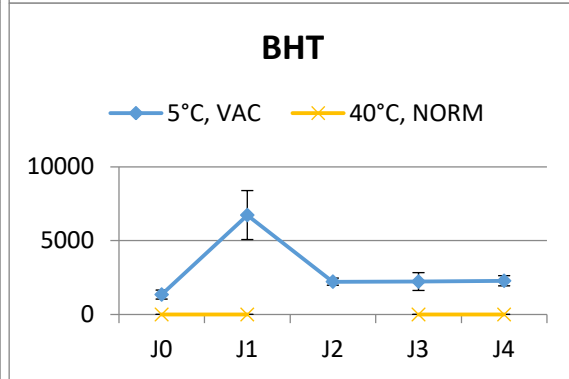
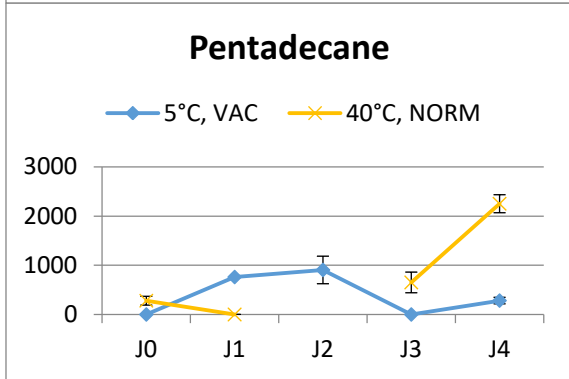
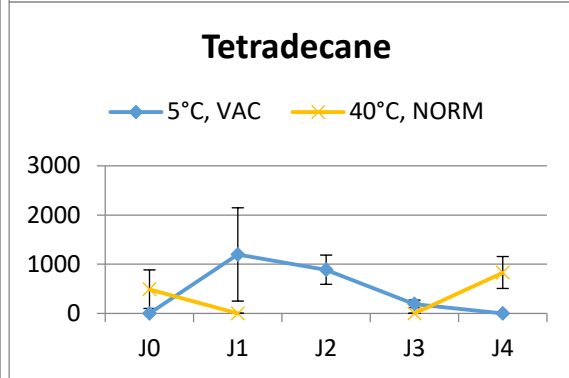
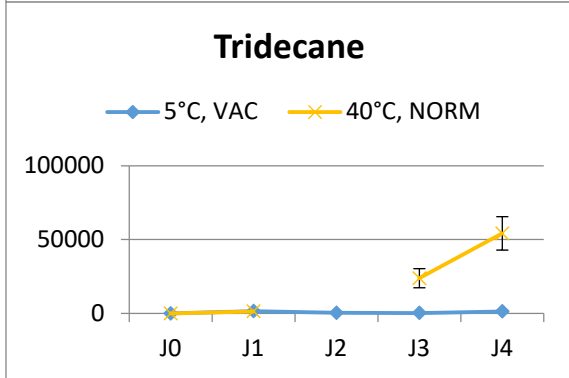
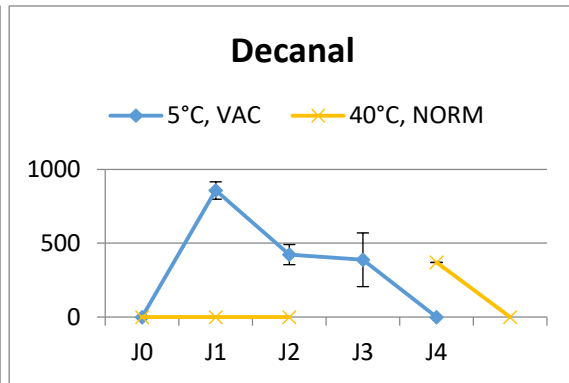
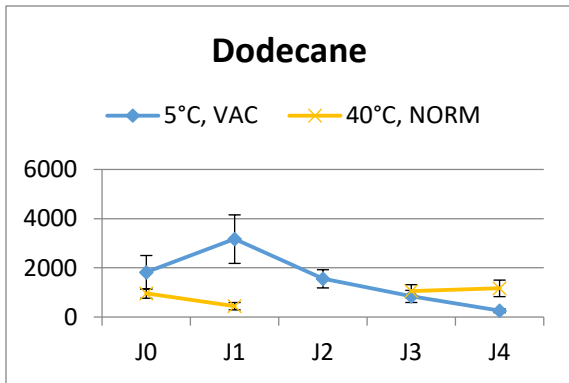




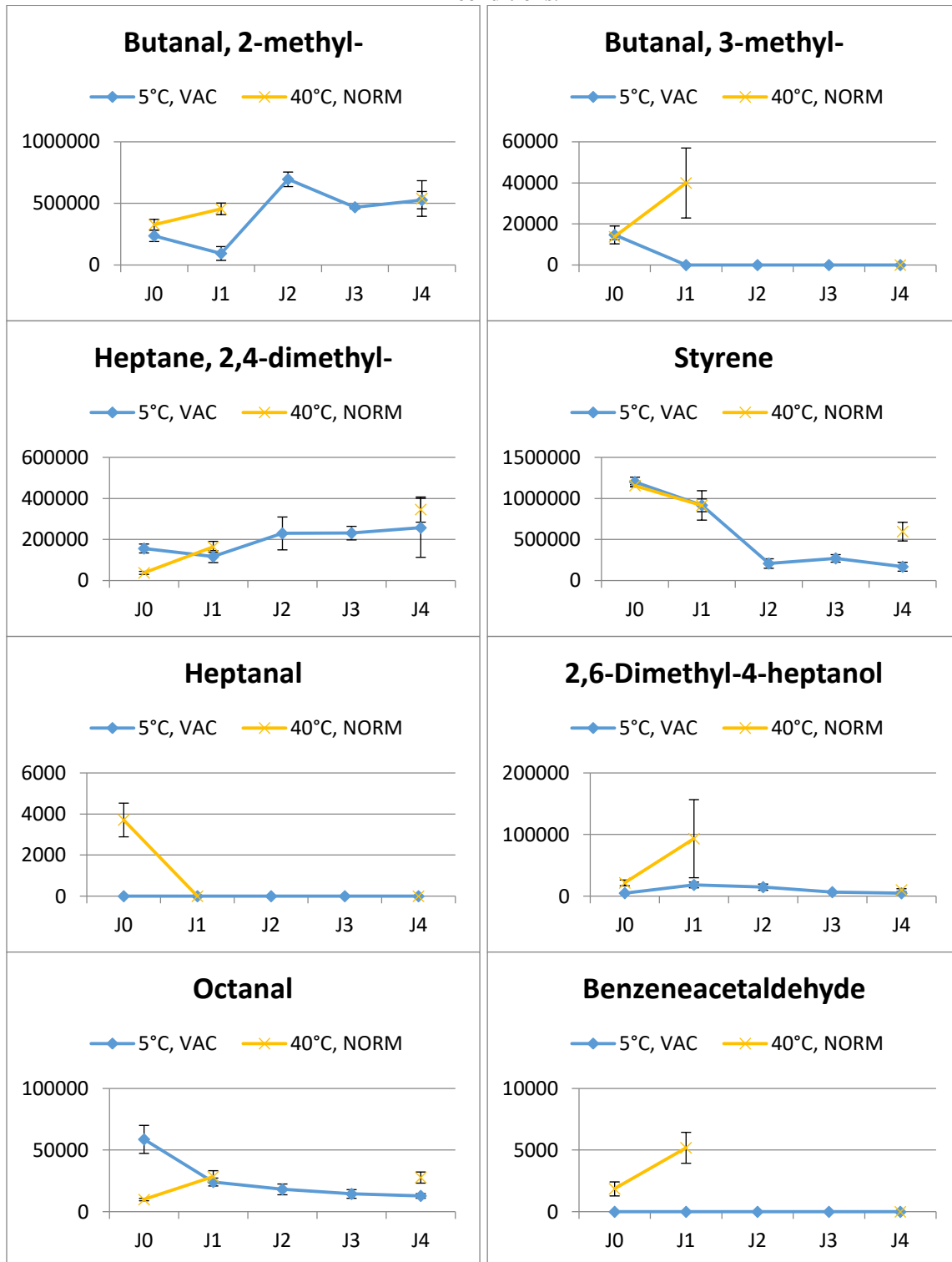


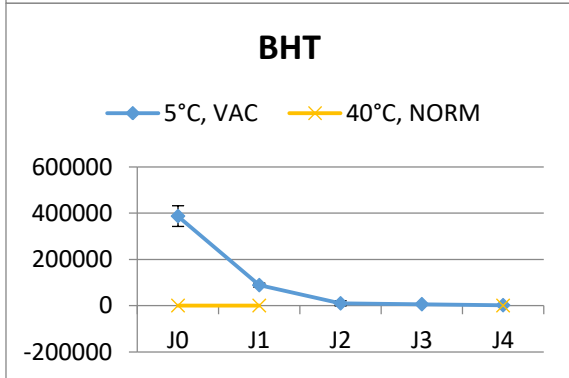
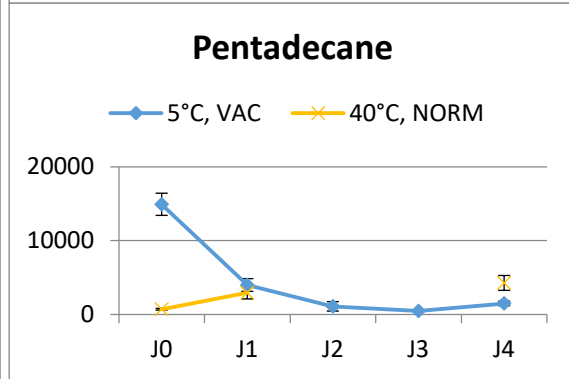
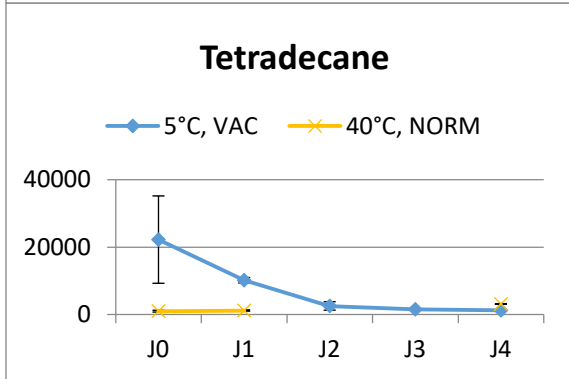
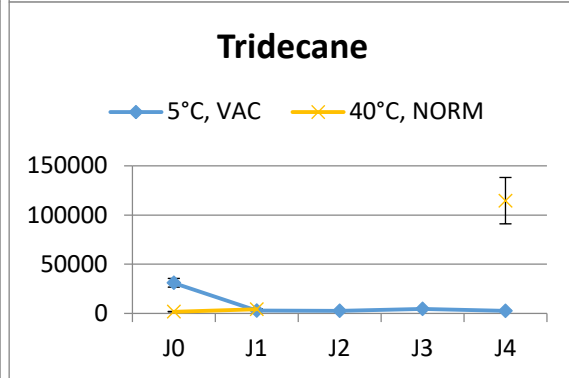
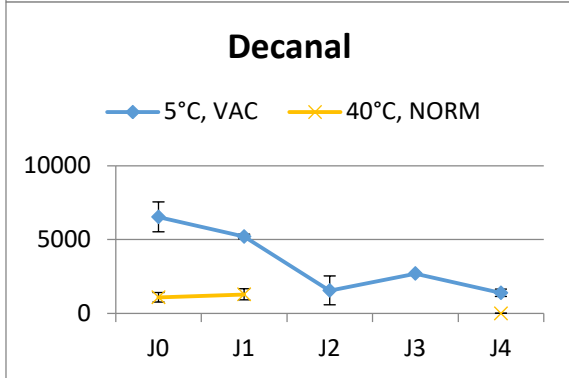
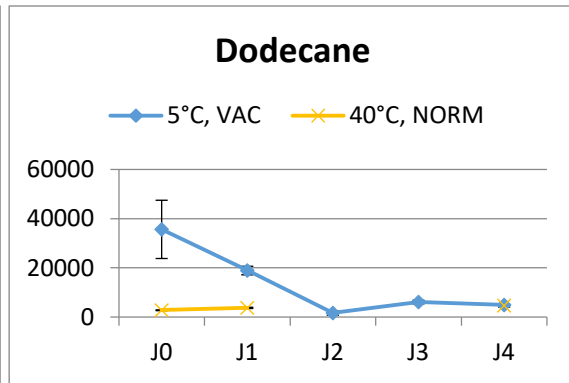
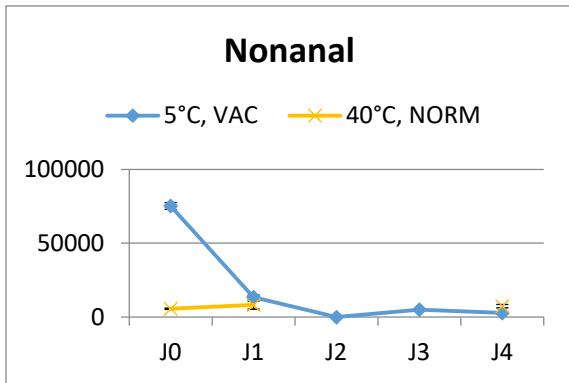
Annex 13: Cod spoilage over 5 days and analyzed at 5°C under vacuum and 40°C with normal conditions.





Annex 14: Pollock spoilage over 5 days and analyzed at 5°C under vacuum and 40°C with normal conditions.





Annex 15: Redfish spoilage over 5 days and analyzed at 5°C under vacuum and 40°C with normal conditions.

