

SILOXANE ANALYSIS IN LANDFILL BIOGAS: STUDY OF SAMPLE CAPTURE METHOD AND IDENTIFICATION – QUANTIFICATION BY HRGC-MS

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IQS TASKS

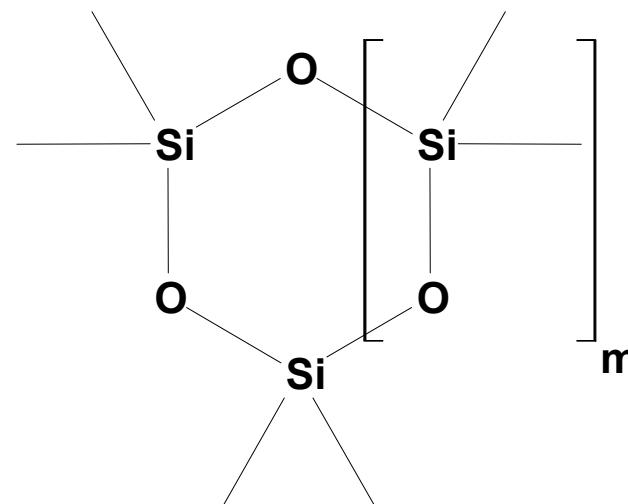
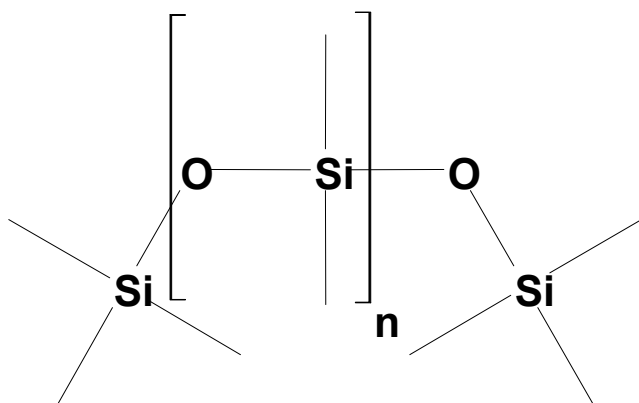
TASK E

- CHROMATOGRAPHIC METHODS.
- CAPTURE METHODS.
- BIOGAS ANALYSIS.

TASK F

- ON-LINE SILOXANE CONTROL SYSTEM.
- ORÍS LANDFILL MONITORING.

SILICON COMPOUNDS



Hexamethyldisiloxane

L2 (M2)

Hexamethylcyclotrisiloxane

D3

Octamethyltrisiloxane

L3 (M2D)

Octamethylcyclotetrasiloxane

D4

Decamethyltetrasiloxane

L4 (M2D2)

Decamethylcyclopentasiloxane

D5

Dodecamethylpentasiloxane

L5 (M2D3)

SILICON COMPOUNDS

Compound Properties

	Boiling Point °C	Molecular weight
L2	101	162.4
D3	134	222.5
L3	153	236.5
D4	176	296.6
L4	194	310.7
D5	210	370.8
L5	232	384.8

IQS TASKS

TASK E

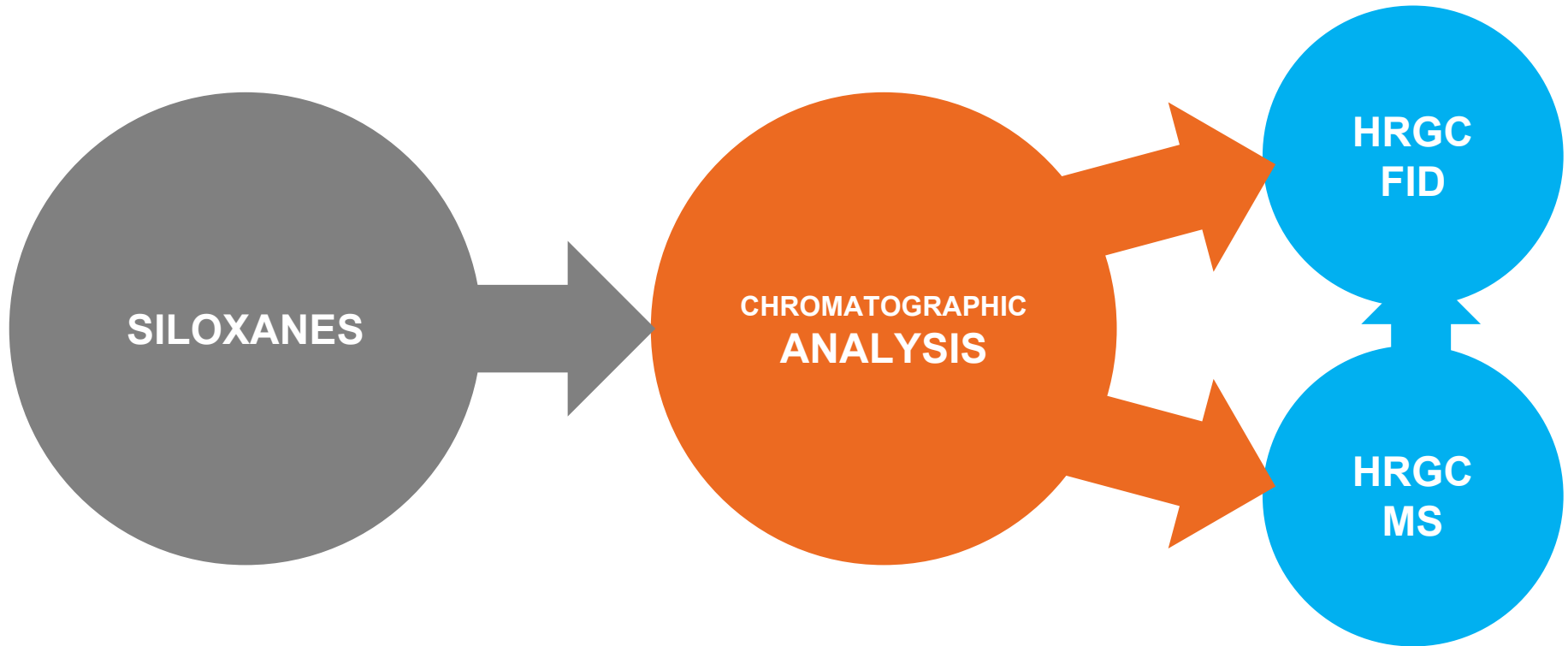
- **CHROMATOGRAPHIC METHODS.**
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TASK F

- ON-LINE SILOXANE CONTROL SYSTEM.
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HRGC Method

Siloxane Analysis



HRGC CHROMATOGRAPHIC PARAMETERS



INJECTION

Injection Volume
2 μ L (liquid)
500 μ L (gas)

Pressure
13 psi

Split /Splitless
12.4 : 1

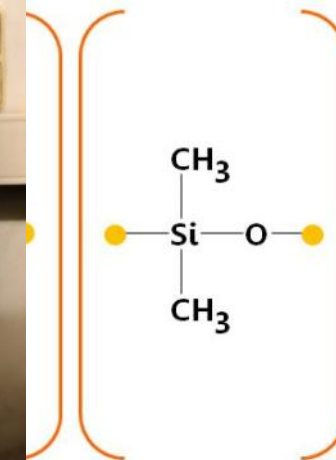
Temperature
250°C

HRGC CHROMATOGRAPHIC PARAMETERS



HP5 – MS

30 m
0.25 mm
0.25 μ m



**95%
Dimethyl
polysiloxane**

MASS SPECTROMETER PARAMETERS

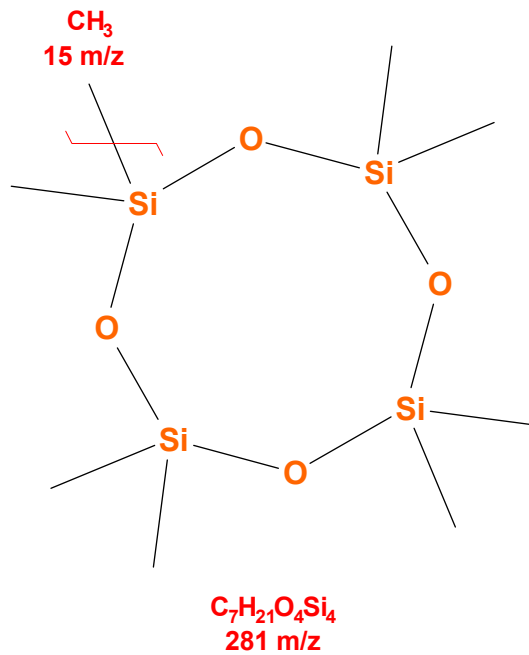


MS Detector

T MS quadrupole
150°C

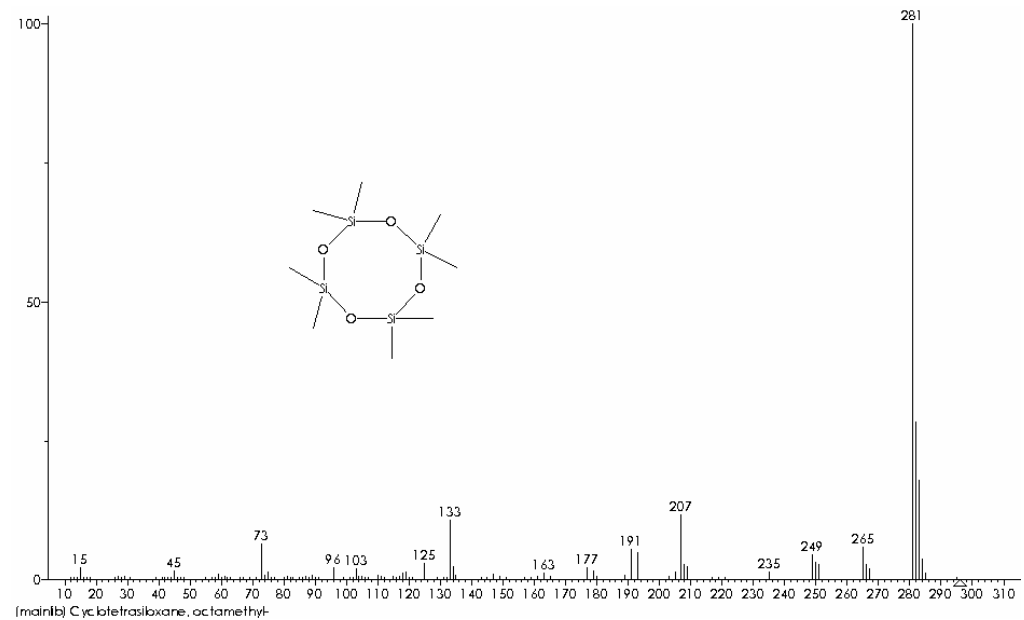
T MS source
230°C

MASS SPECTROMETER PARAMETERS

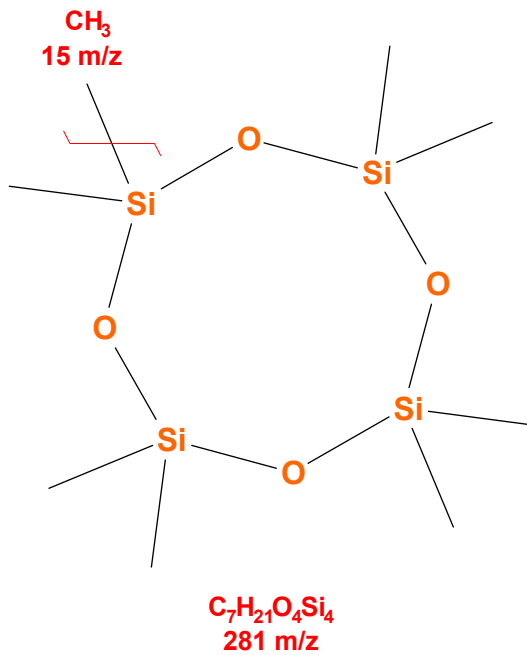


Siloxane - D4
296 amu

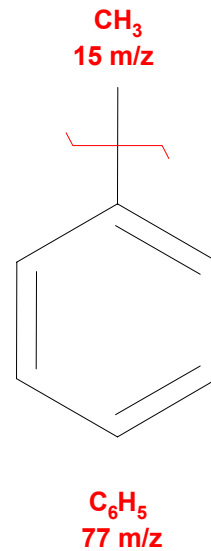
SILOXANE - D4 - MASS SPECTRUM



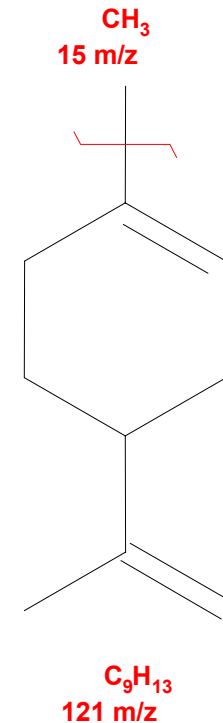
MASS SPECTROMETER PARAMETERS



Siloxane - D4
296 amu

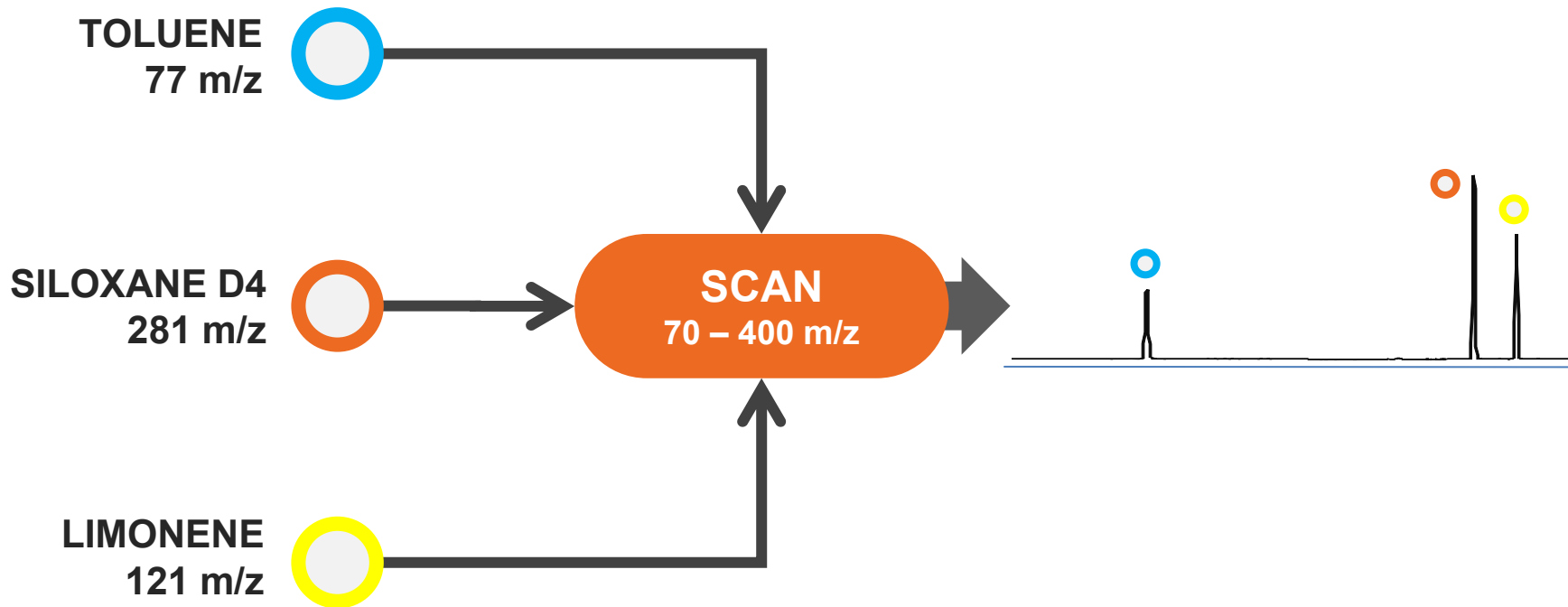


Toluene
92 amu





Limonene
136 amu

MASS SPECTROMETER PARAMETERS



MASS SPECTROMETER PARAMETERS

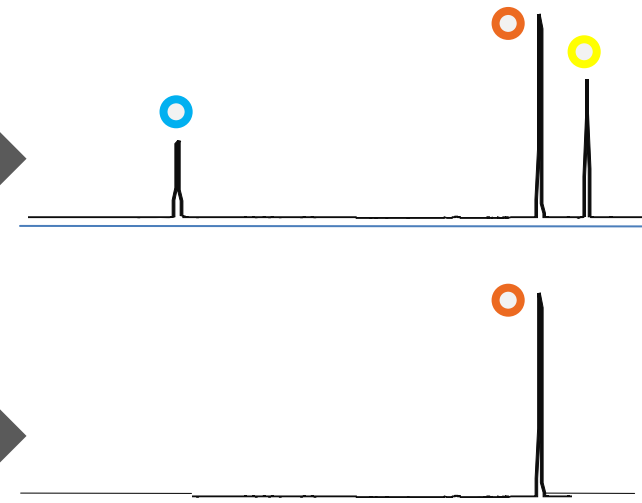
TOLUENE 
77 m/z

SILOXANE D4 
281 m/z

LIMONENE 
121 m/z

SCAN
70 – 400 m/z

SIM
281 m/z



MASS SPECTROMETER PARAMETERS

SCAN

Low Mass	70.0 m/z
High Mass	400.0 m/z

SIM

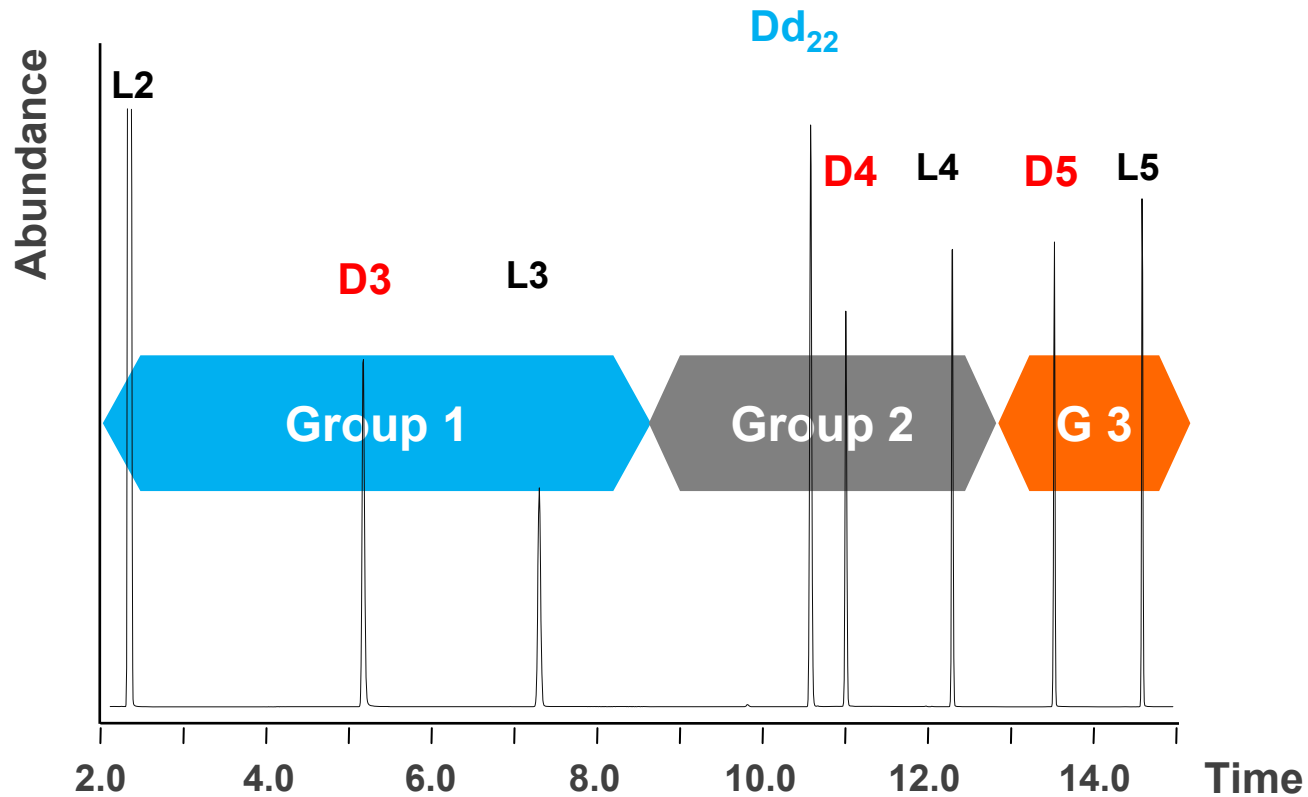
Group 1	L2; D3; L3
Ions	73, 147, 191, 205, 207, 221 m/z
Dwell	25

Group 2	D-d₂₂ (Decane-d ₂₂); D4; L4
Ions	73, 82, 133, 164, 207, 265, 281, 295 m/z
Dwell	25

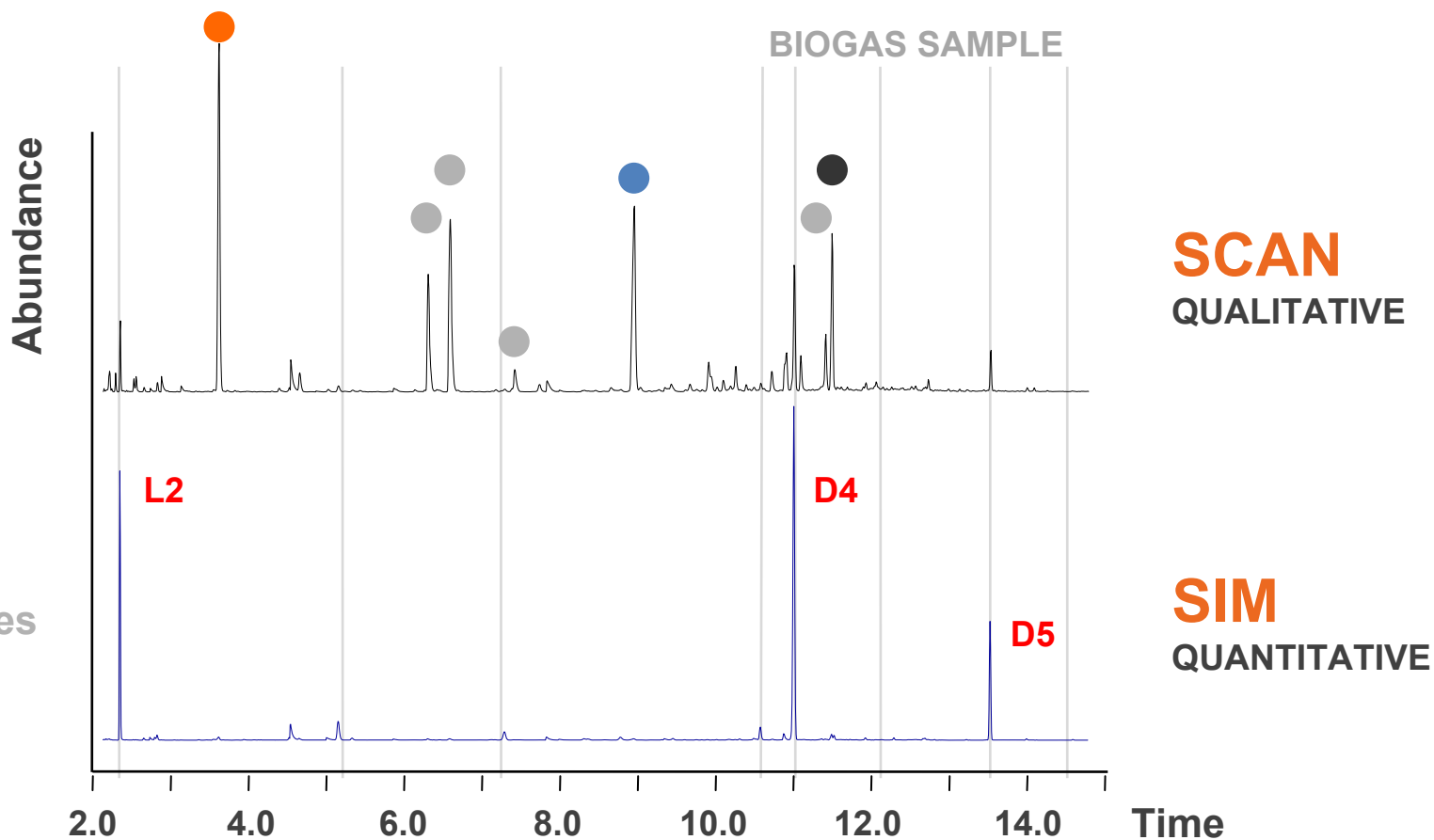
Group 3	D5; L5
Ions	73, 147, 267, 281, 355, 369 m/z
Dwell	25

MASS SPECTROMETER PARAMETERS

SIM Ions Group



CHROMATOGRAMS ACQUISITION SCAN – SIM MODE

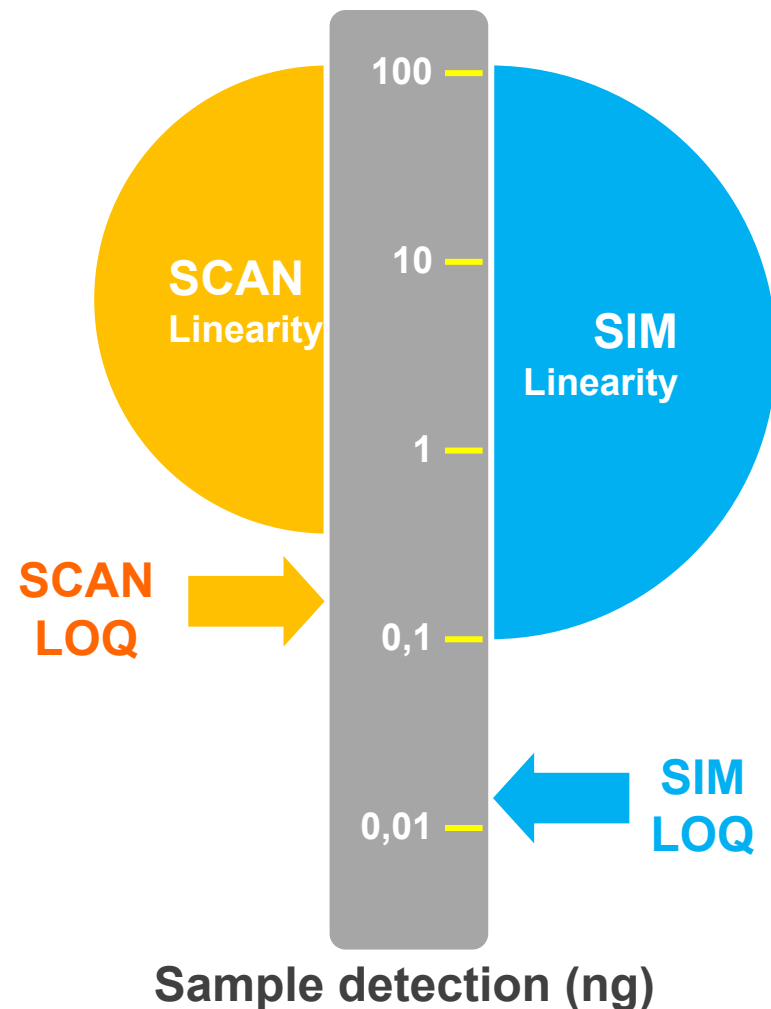


HRGC Method

Siloxane Analysis

METHOD VALIDATION

	SCAN	SIM
Selectivity	!	!!!
Limit of Quantification	0.4 ng	0.04 ng
Repeatability RSD (%)	4%	2%
Linearity r^2	0.999	0.999



IQS TASKS

TASK E

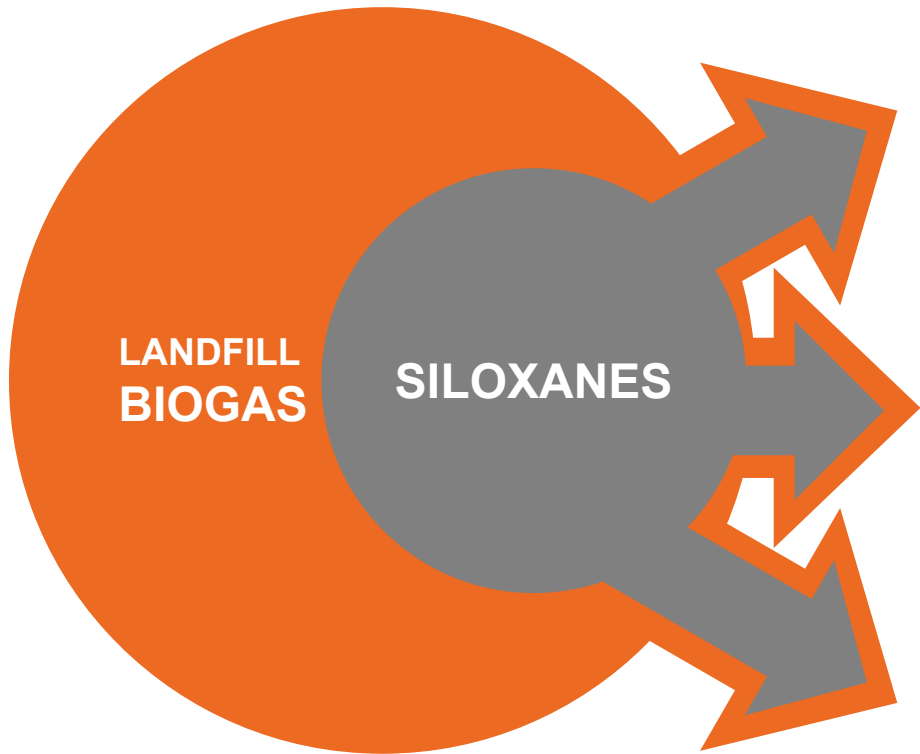
- CHROMATOGRAPHIC METHODS.
- **CAPTURE METHODS.**
- BIOGAS ANALYSIS.

TASK F

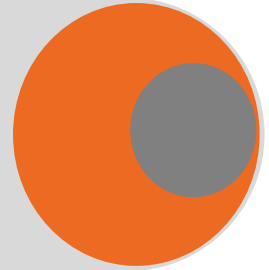
- ON-LINE SILOXANE CONTROL SYSTEM.
- ORÍS LANDFILL MONITORING.

Capture Method

Siloxane Analysis



**Tedlar™
BAG**



**IMPINGERS
with Solvent**



**Adsorbent
TUBES**



ALTERNATIVE CAPTURE METHODS

Tedlar™ BAG



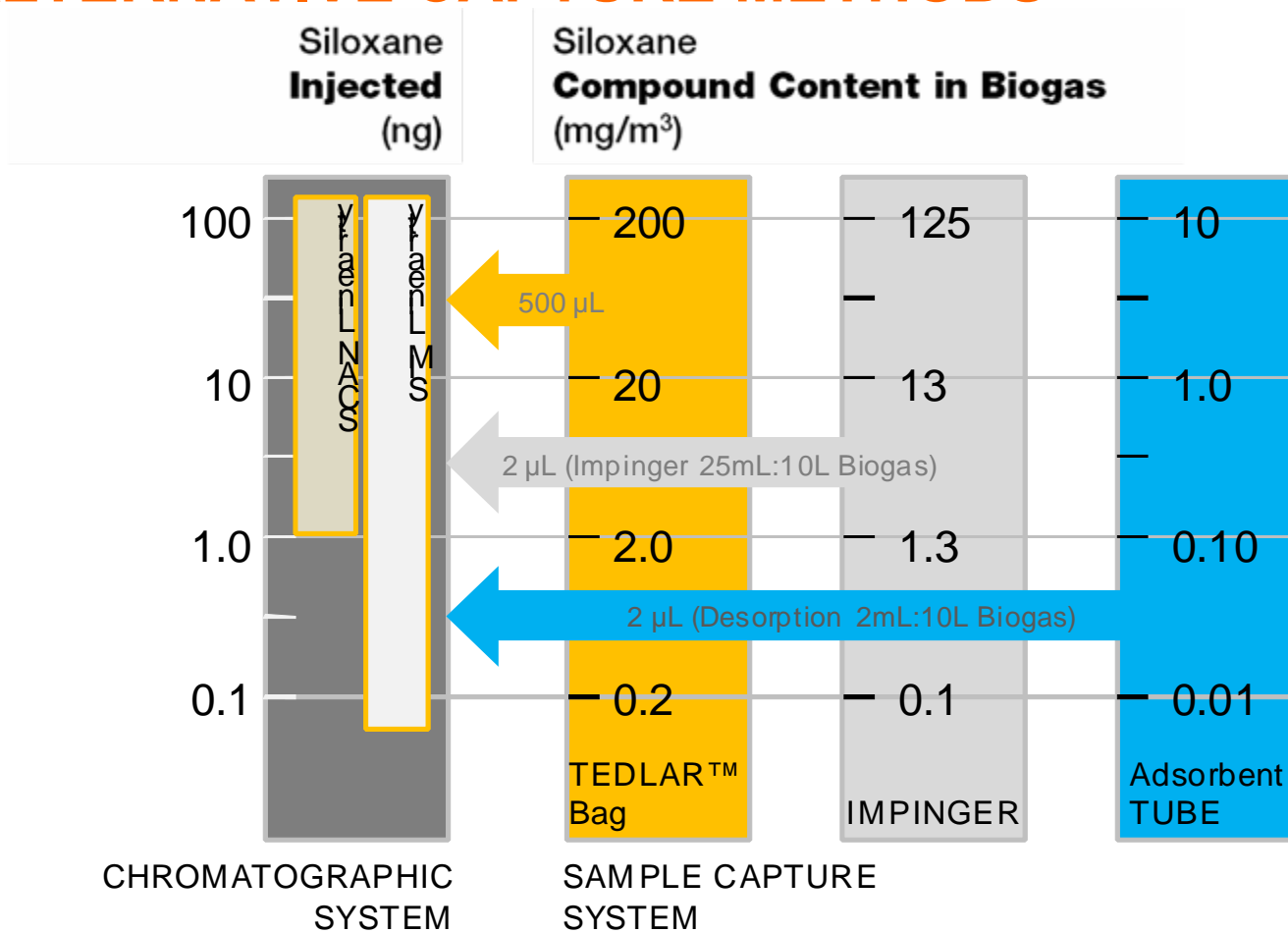
IMPINGER



Adsorbent TUBE



ALTERNATIVE CAPTURE METHODS



ALTERNATIVE CAPTURE METHODS COMPARATIVE RESULTS

July 2006	Tedlar BAGS	IMPINGER	Adsorbent TUBES
	Tedlar™	Hexane as solvent	Anasorb®747
	mg/m ³	mg/m ³	mg/m ³
L2	1.5	2.4	2.5
D3	2.5	1.0	1.0
L3	<0.2	<0.1	0.05
D4	6.0	8.2	6.4
L4	<0.2	<0.1	0.01
D5	1.5	1.8	1.8
L5	<0.2	<0.1	<0.01
TOTAL	11.5	13.4	11.8

SOLID ADSORBENT TUBES – POLYMERIC BASED

ORBO®706



Bed A : Bed B 200 : 100 mg

Adsorbent SDVB

Particle Size 20 - 40 MESH

Homogeneity HIGH

ORBO®43



200 : 100 mg

SDVB

20 - 40 MESH

MEDIUM

ORBO®402



200 : 100 mg

TENAX

36 - 60 MESH

VERY LOW

SOLID ADSORBENT TUBES – CARBON BASED

ORBO®32

ANASORB®747

ORBO®101



Bed A : Bed B 100 : 50 mg
 400 : 200 mg

Adsorbent ACTIVATED CHARCOAL

Particle Size 20 - 40 MESH
 20 µm

Homogeneity VERY LOW

400 : 200 mg

ACTIVATED CHARCOAL

20 - 40 MESH
 50 µm

HIGH

100 : 50 mg

GRAPHITE

20 - 40 MESH
 20 µm

LOW

COMPARISON OF DIFFERENT SOLID ADSORBENTS

July 2006	Polymeric Based	Carbon Based
	ORBO®706 Chromosorb102	ANASORB®747 Activated Charcoal
	mg/m³	mg/m³
L2	0.32	2.5
D3	0.43	1.0
L3	0.11	0.05
D4	5.5	6.4
L4	<0.01	0.01
D5	1.9	1.8
L5	<0.01	<0.01
TOTAL	8.3	11.8

COMPARISON OF DIFFERENT ACTIVATED CHARCOALS

March 2007

Carbon Based

	ORBO®32 Activated Charcoal	ANASORB®747 Activated Charcoal
	mg/m³	mg/m³
L2	2.4	2.5
D3	1.07	1.03
L3	0.14	0.15
D4	3.6	3.9
L4	<0.02	<0.02
D5	0.28	0.29
L5	<0.02	<0.02
TOTAL	7.5	7.8

Notes

Adsorbed Siloxanes in bed B are negligible.

Samples repeatability is better than 5%.

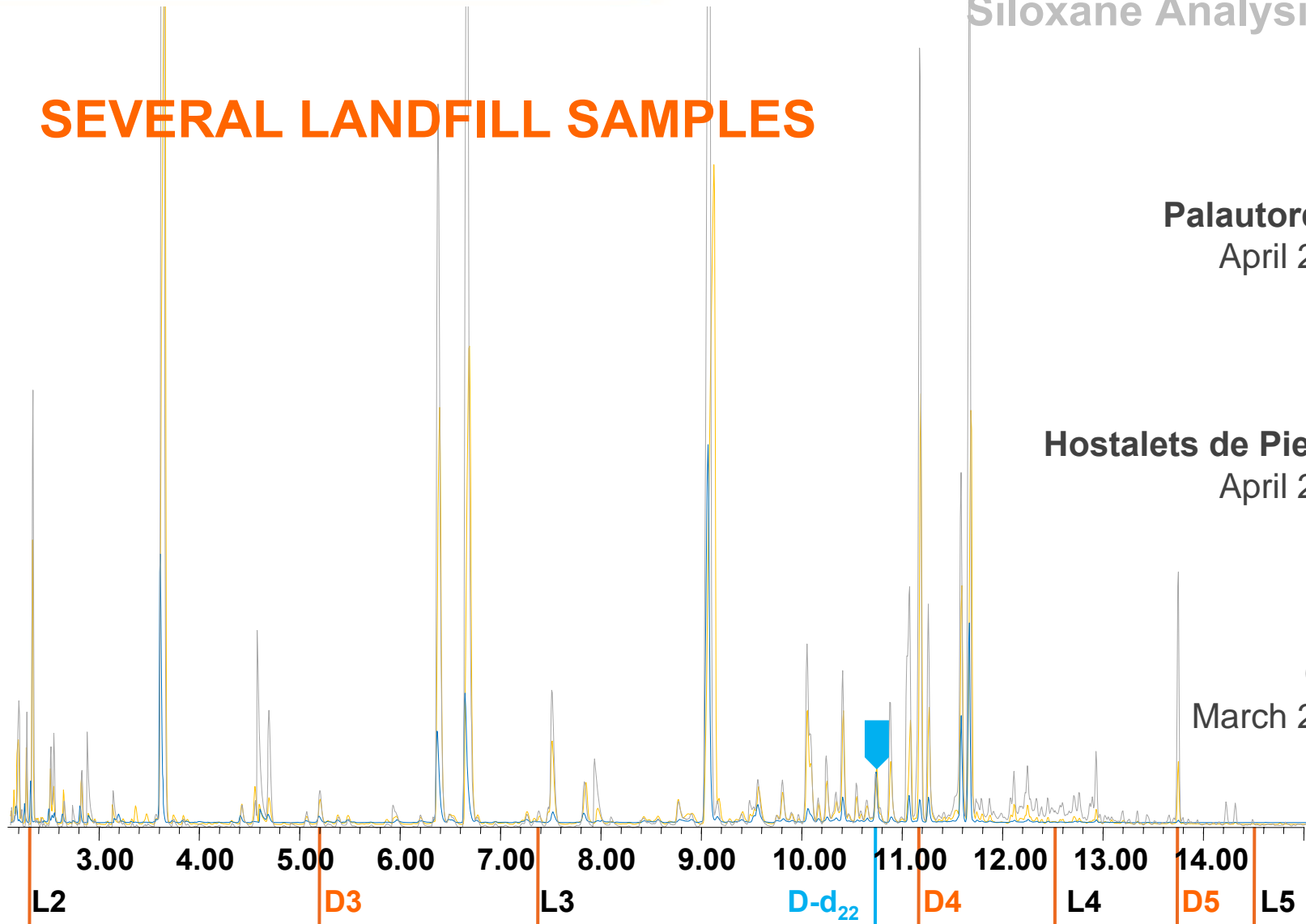
SEVERAL LANDFILL SAMPLES



Capture Method

Siloxane Analysis

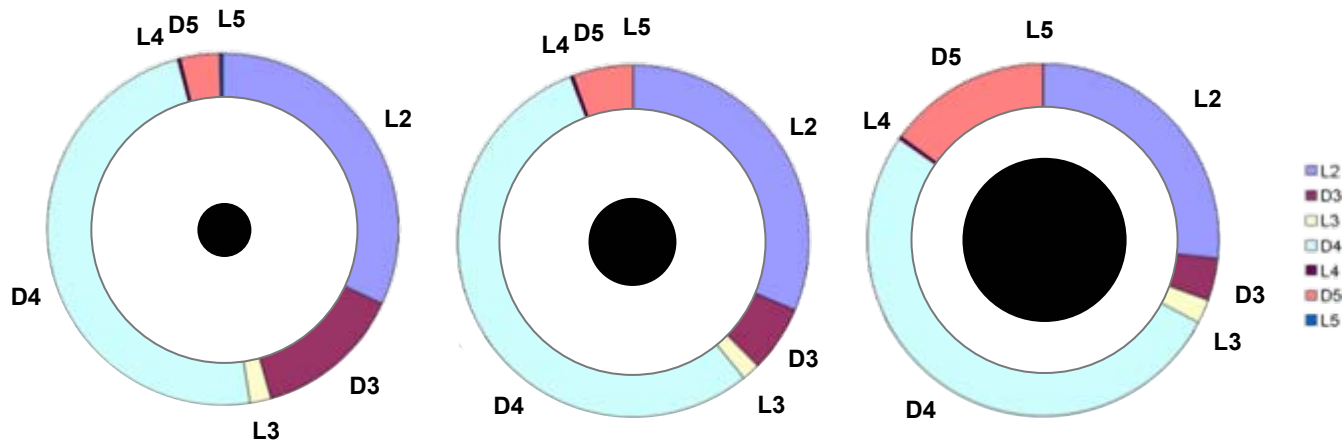
SEVERAL LANDFILL SAMPLES



SEVERAL LANDFILL SAMPLES

	Urban Landfill	Industrial & Urban Landfill	
	ORÍS	HOSTALETS DE PIEROLA	PALAUTORDERA
	mg/m ³	mg/m ³	mg/m ³
L2	2.5	6.6	21
D3	1.0	1.3	3.2
L3	0.14	0.38	1.7
D4	3.8	12	41
L4	<0.02	<0.02	0.17
D5	0.29	1.0	12
L5	<0.02	<0.02	0.06
TOTAL	7.7	21	79

SEVERAL LANDFILL SAMPLES



**ORÍS
 LANDFILL**


Siloxanes in Biogas
 Total Content
7.7 mg/m³

**HOSTALETS DE PIEROLA
 LANDFILL**

Siloxanes in Biogas
 Total Content
21 mg/m³

**PALAUTORDERA
 LANDFILL**

Siloxanes in Biogas
 Total Content
79 mg/m³

 The Inner Circle
 Proportional area to
 The total siloxanes
 Content in biogas.

Task E

Siloxane Analysis

- The procedure developed in Task E is adequate for the siloxanes analysis in different landfill's biogas in a wide concentration range.
- The procedure developed includes siloxane absorption step using activated charcoal, siloxane desorption with hexane, and analysis by HRGC-MS (SIM/SCAN).

IQS TASKS

TASK E

- CHROMATOGRAPHIC METHODS.
- CAPTURE METHODS
- BIOGAS ANALYSIS.

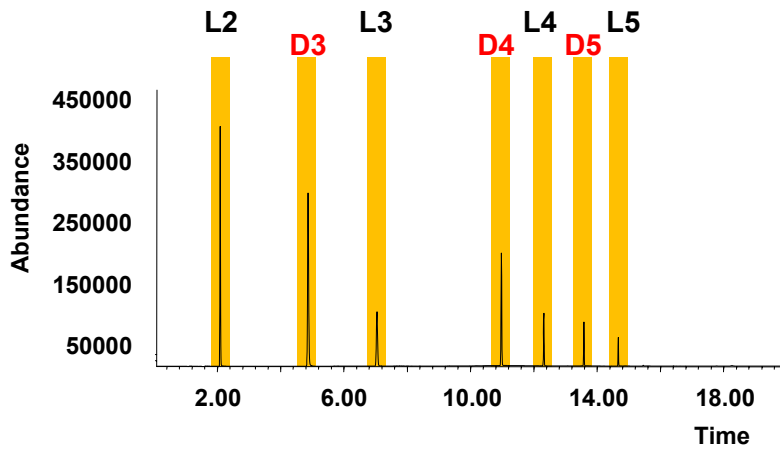
TASK F

- **ON-LINE SILOXANE CONTROL SYSTEM.**
- ORÍS LANDFILL MONITORING.

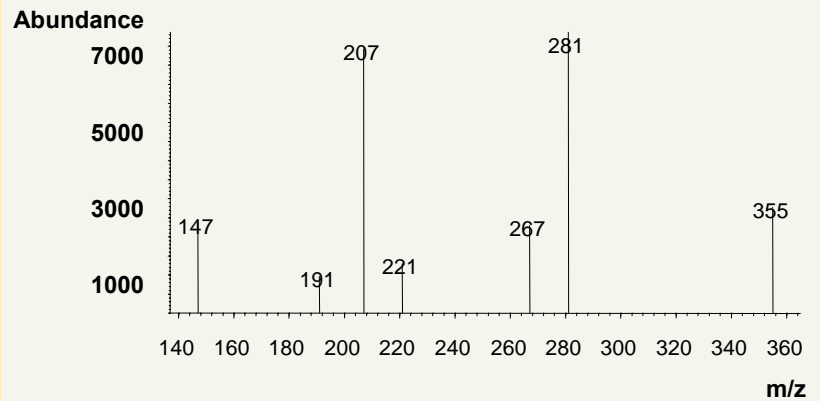
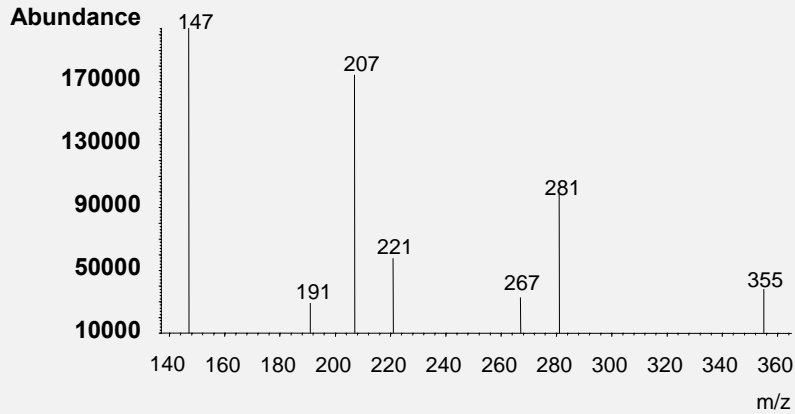
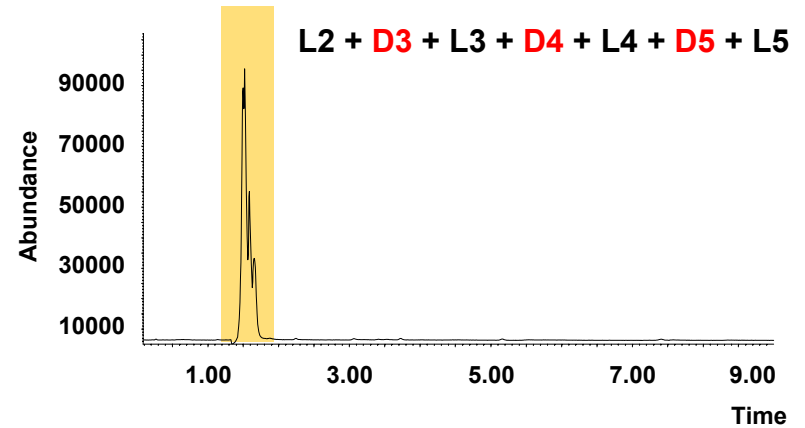
- MS** Mass Spectrometer
- AES** Atomic emission spectroscopy
Silicon wavelength detection
- NDIR** Photo Acoustic
Infrared Spectroscopy
- FTIR** Fourier Transform
Infrared Spectroscopy

On-line Control Siloxane Analysis

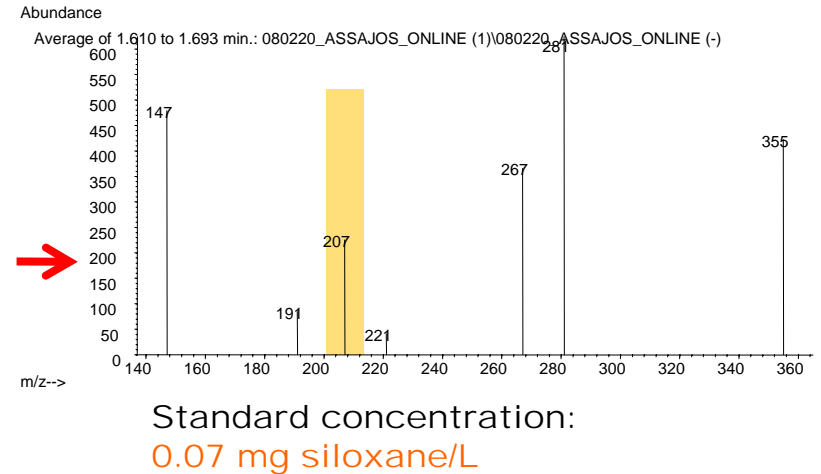
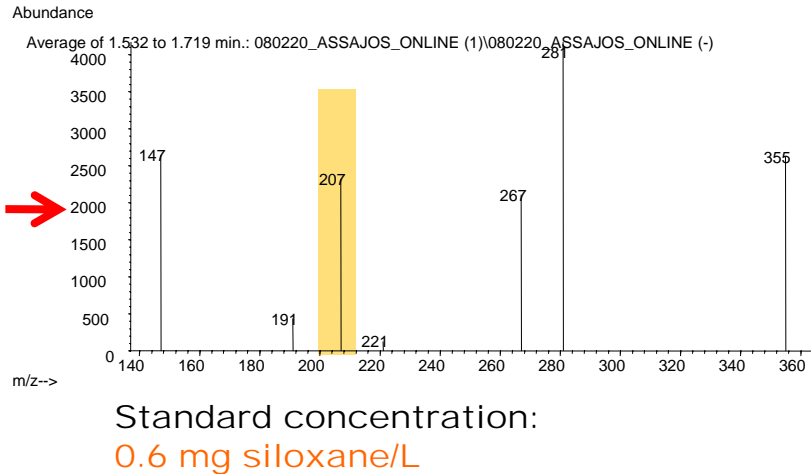
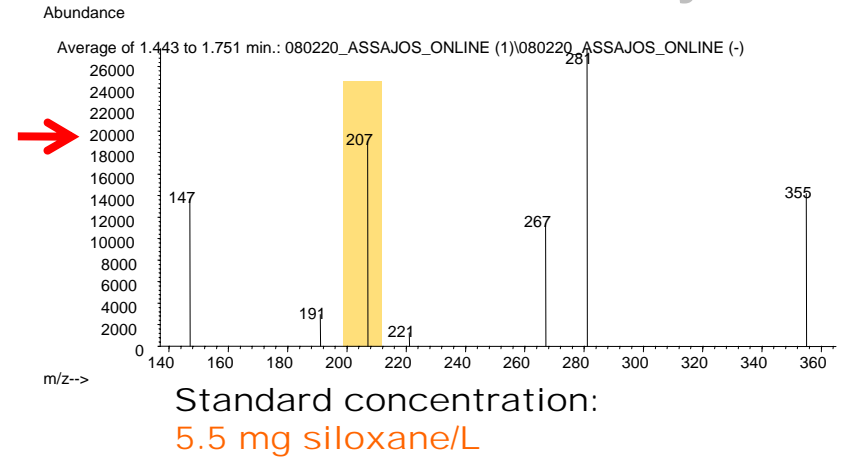
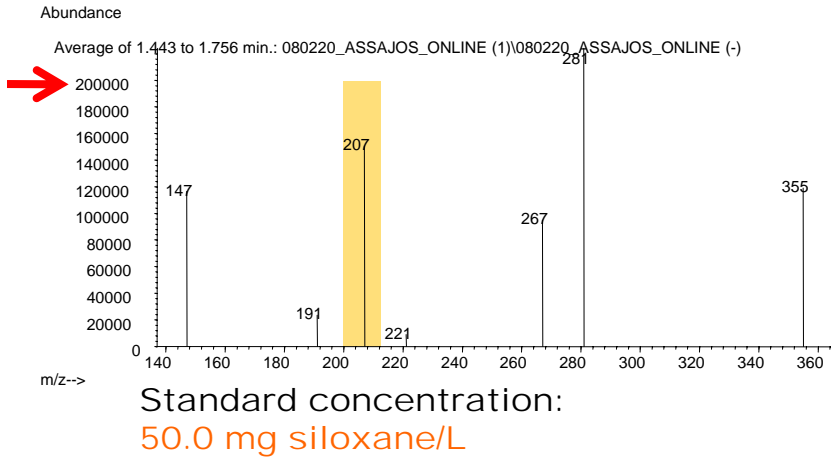
HRGC MS



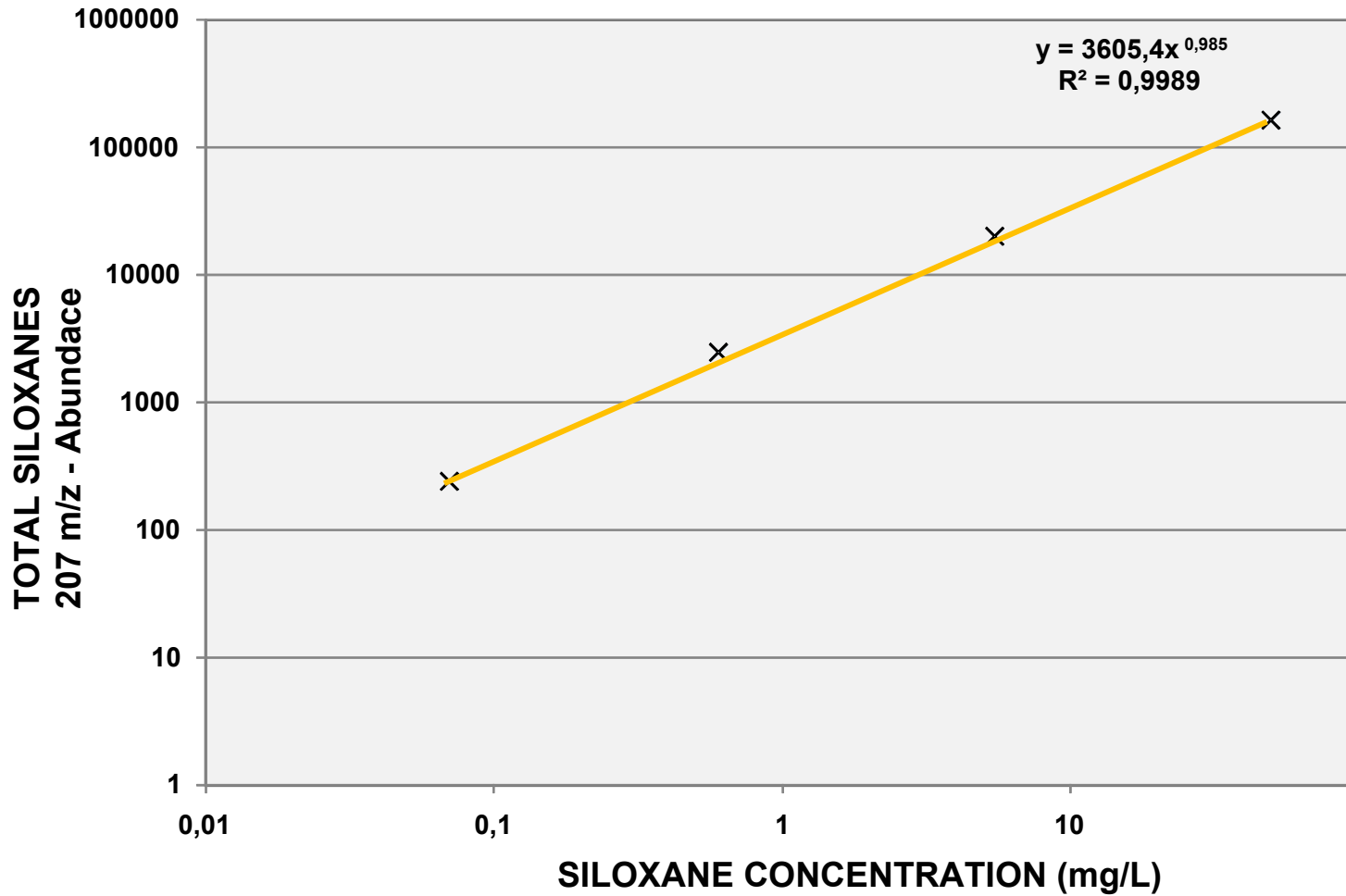
Direct Injection MS



On-line Control Siloxane Analysis



On-line Control Siloxane Analysis



IQS TASKS

TASK E

- CHROMATOGRAPHIC METHODS.
- CAPTURE METHODS.
- BIOGAS ANALYSIS.

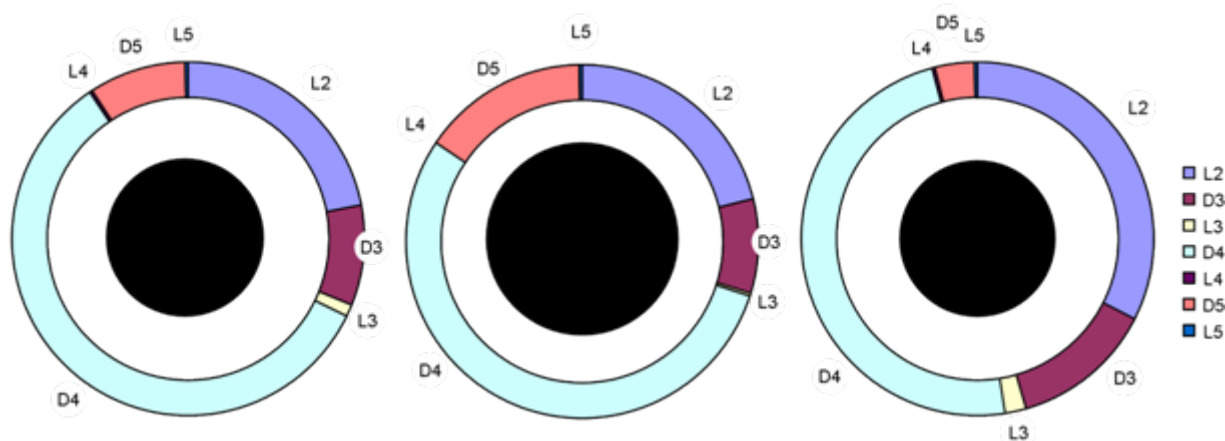
TASK F

- ON-LINE SILOXANE CONTROL SYSTEM.
- **ORÍS LANDFILL MONITORING.**

SILOXANES CONTENT: ORÍS SAMPLES I



SILOXANES CONTENT: ORÍS SAMPLES I



march, 18th 2006


Siloxanes in Biogas
 Total Content
7.7 mg/m³

july, 24th 2006

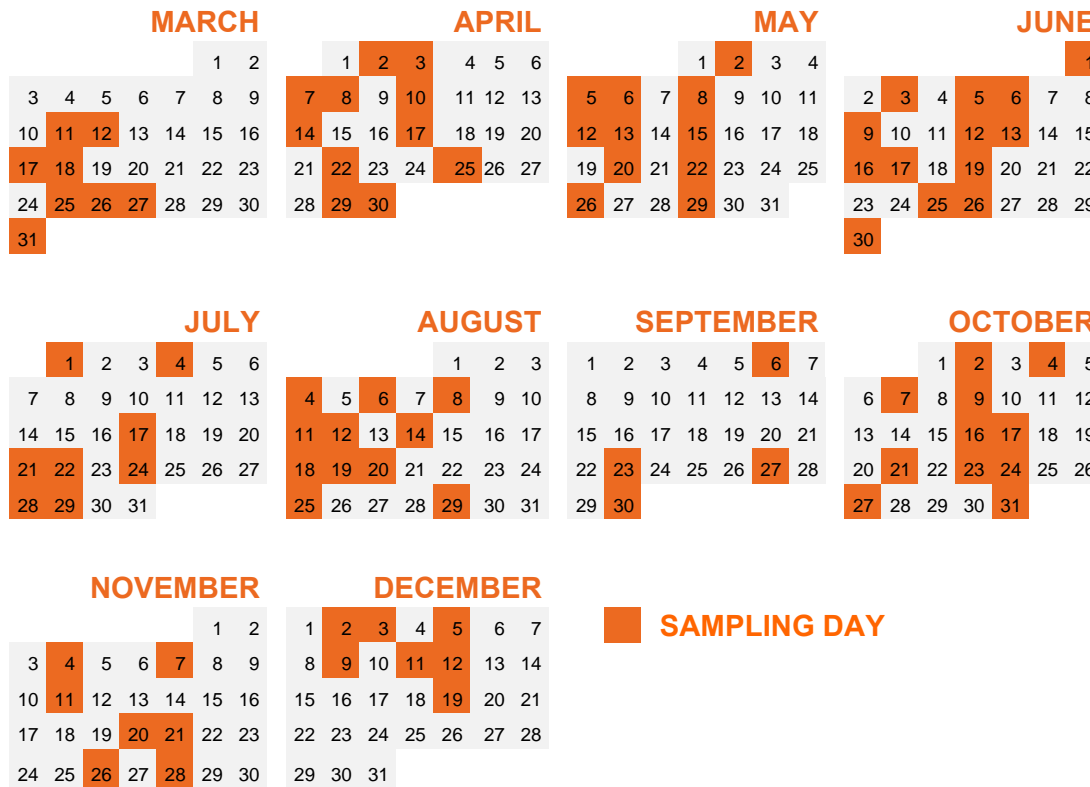
Siloxanes in Biogas
 Total Content
12 mg/m³

march, 22th 2007

Siloxanes in Biogas
 Total Content
7.7 mg/m³

 **The Inner Circle**
 Proportional area to
 The total siloxanes
 Content in biogas.

ORÍS SAMPLES II: SEVERAL SAMPLING POINTS

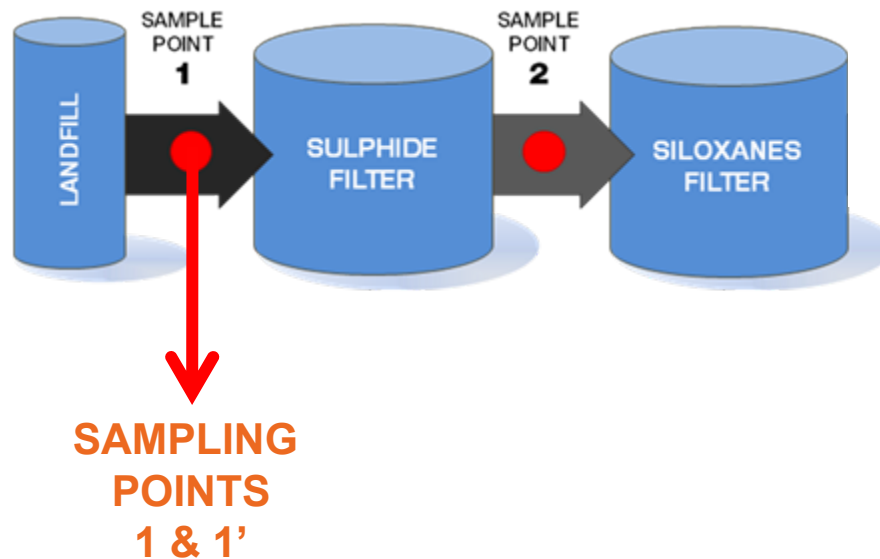


Samples from Orís
 (CESPA Landfill)

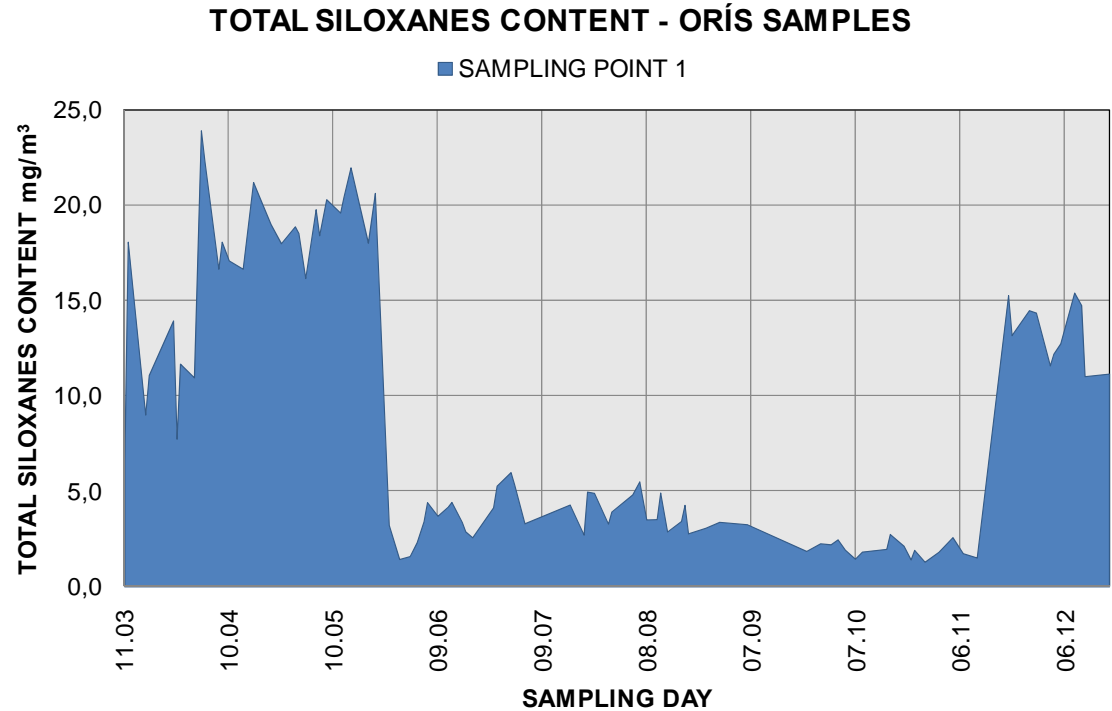
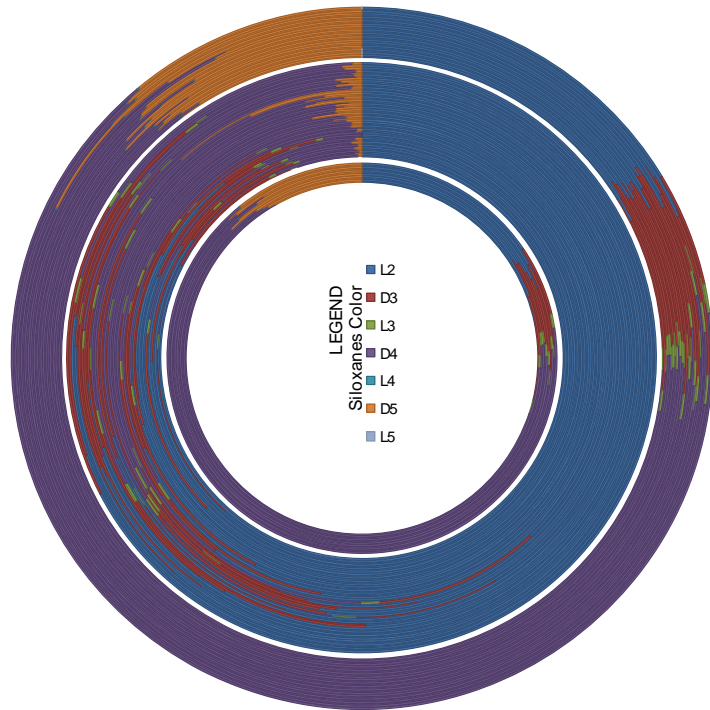
Sampling done
 by PROFACOR

Samples analyzed
 by IQS

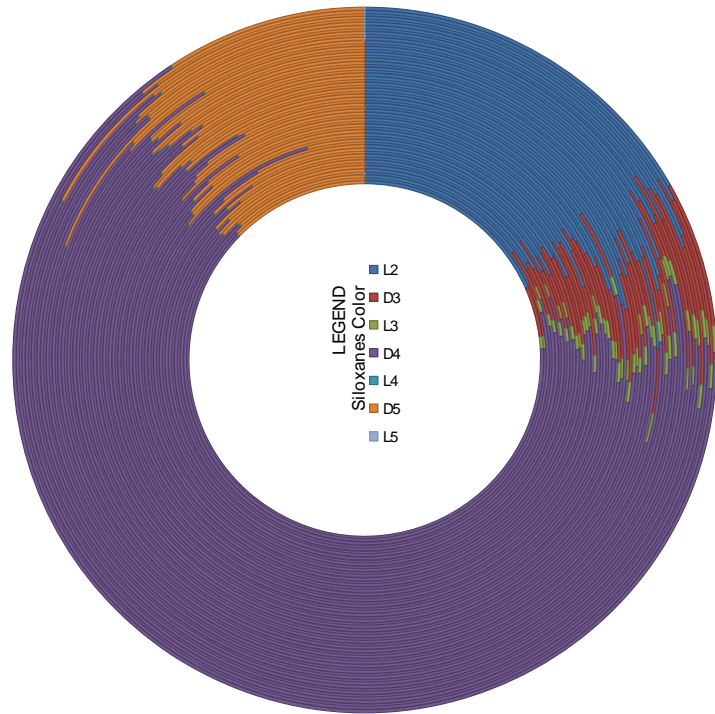
ORÍS SAMPLES II: SAMPLING POINTS



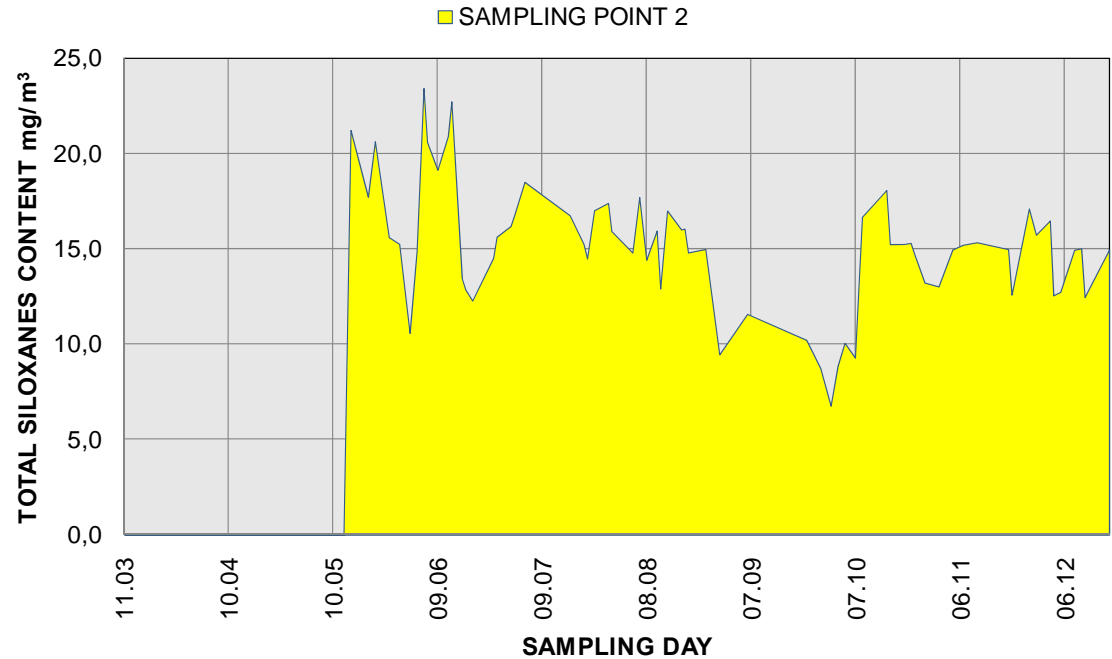
ORÍS SAMPLES II: SAMPLING POINT 1



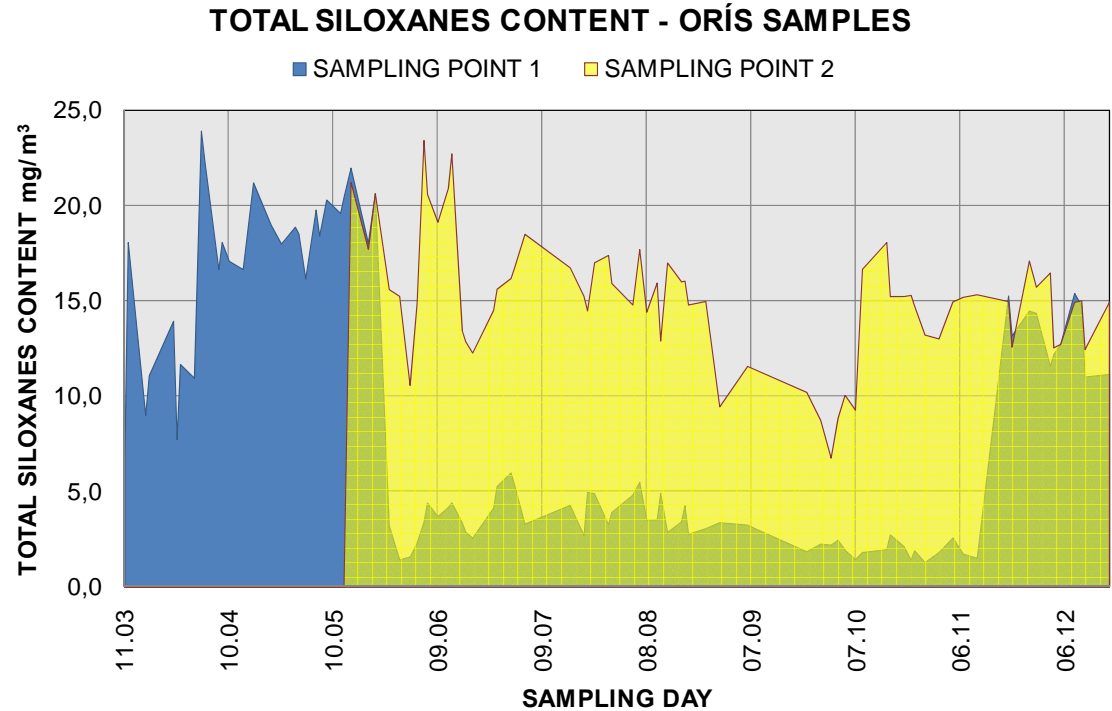
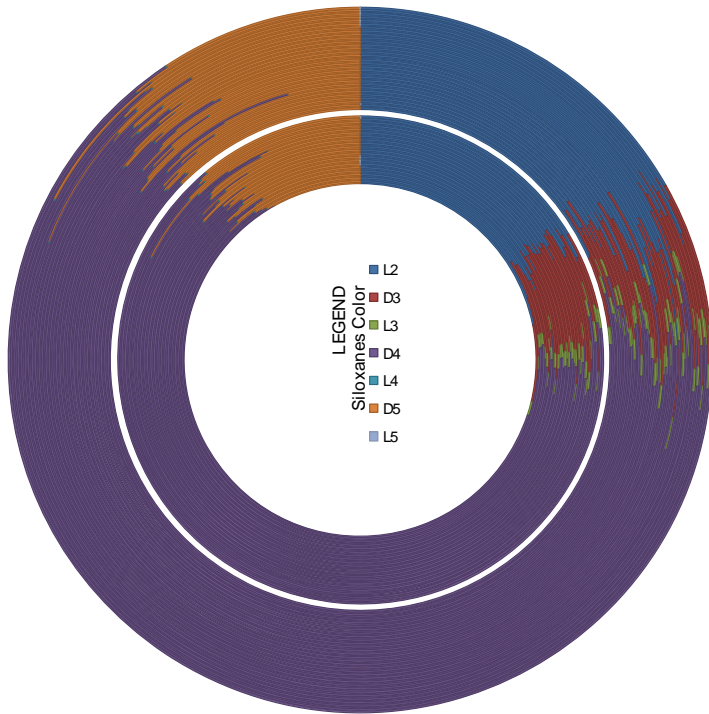
ORÍS SAMPLES II: SAMPLING POINT 2



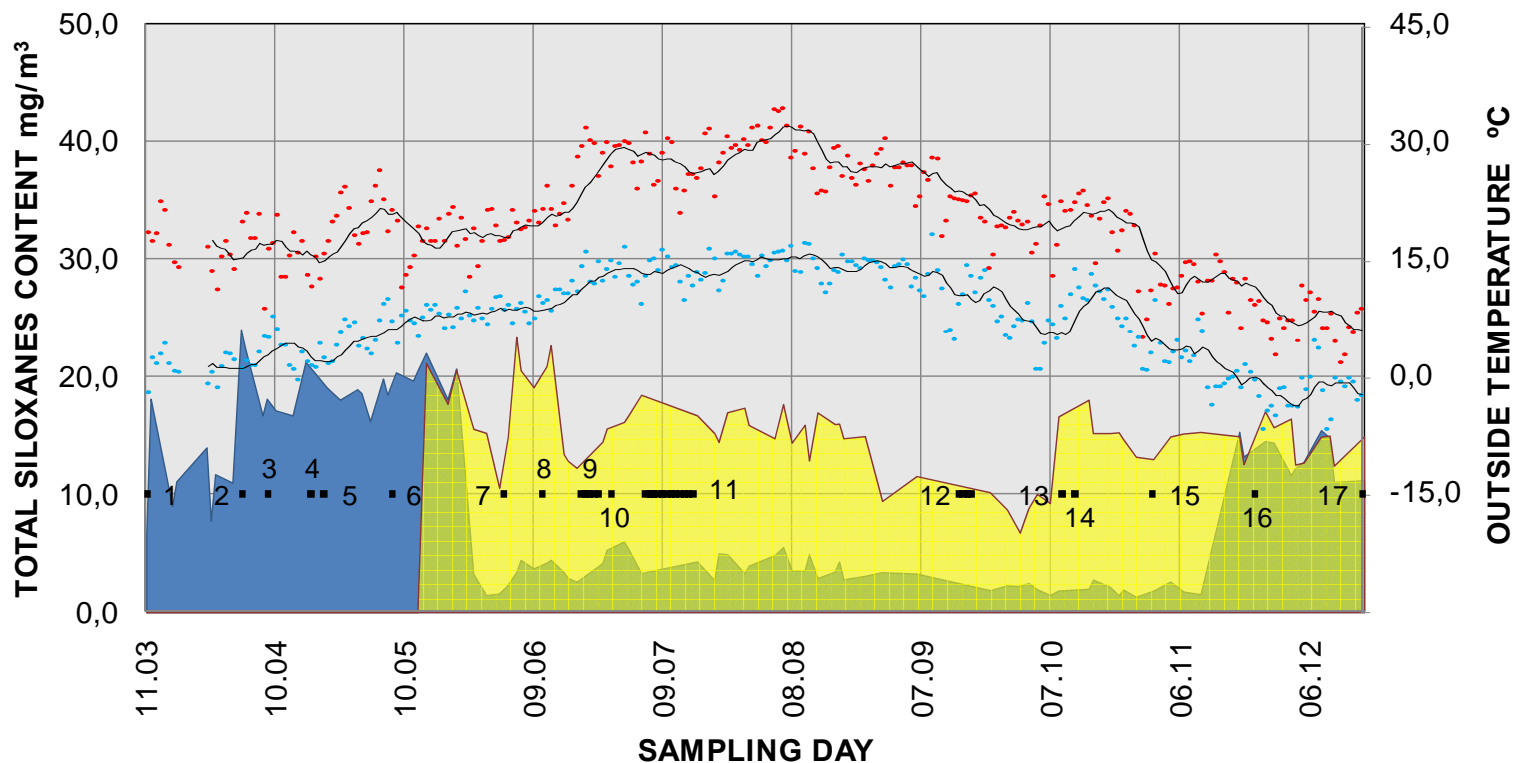
TOTAL SILOXANES CONTENT - ORÍS SAMPLES



ORÍS SAMPLES II: SAMPLING POINT 1 & 2



ORÍS SAMPLES II: SAMPLING POINT 1 & 2 and DAILY TEMPERATURES



- Daily minimum temperature
- Daily maximum temperature
- Biogas extraction stop

Task F

Siloxanes Analysis

- **Siloxanes concentration** in Orís biogas has been maintained at the same level during the study. Moreover, the proportion among the seven siloxanes has also been constant.
- The results presented indicate that it is not essential to install a **on-line monitoring** system for siloxanes analysis in Orís landfill.



SILOXANE ANALYSIS IN LANDFILL BIOGAS: STUDY OF SAMPLE CAPTURE METHOD AND IDENTIFICATION – QUANTIFICATION BY HRGC-MS

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