



Generation of standards from a mixture of hydrocarbons with LiqMix™ Cascade

LiqMix™ Cascade, a calibration gas generator

Some applications require gas standards that are not available in cylinders or a large number of mixtures at various concentrations.

The LiqMix™ Cascade generator, developed by AlyTech, produces these standard gases from pure liquids or mixtures by vaporizing the liquid phase in a gas stream, with the possibility of adding other standard gases to this mixture.



Liquid and gas flow rates are controlled automatically, with very high precision and can vary over a wide range. This allows the faithful and accurate generation of a gas mixture at the desired concentration.

The dedicated software allows you to create sequences and can be automatically synchronized with third-party instruments such as a GC, a μ GC, a spectrometer, a gas analyser, or any other instrument.

LiqMix™ Cascade is a simple and effective tool for performing multipoint calibrations, linearity checks and LOD/LOQ validations. It is also used to reproduce an industrial gas mixture to study the feasibility and stability of analysers. It allows working with mixtures such as BTEX, other volatile hydrocarbons, water, siloxanes, ethanol, phenol, or any other organic compound.

Generation of standard gases

This study describes an analytical method for rapidly calibrating a GC-FID with standards generated by LiqMix™ Cascade. To avoid high costs, long delivery times and short shelf life of gas cylinders, the standards containing the hydrocarbons were prepared on site using an AlyTech LiqMix™ Cascade. The calibration was carried out using an equal volume mixture of 3 compounds: Hexane, Octane and Decane.

The various components of the LiqMix™ Cascade were temperature-regulated to allow the vaporization and maintenance of the mixture of hydrocarbons in the gaseous phase. The table below shows the temperature setpoints associated with the generation of hydrocarbon standards presented in the following chapter.

Components	Temperature
Evaporator	60°C
Mixing chamber	60°C
Heated lines	60°C

Table 1: Heating parameters used for the hydrocarbon mixture.

Once the sequence was configured and launched, the desired mixture(s) were obtained at the output of LiqMix™ Cascade.

Example of generation of standards from a mixture of hydrocarbons with LiqMix™ Cascade

Axel'One's R&D laboratory is dedicated to industrial analysis and provides online analysis solutions for a consortium of manufacturers. Equipped with analysers such as chromatographs, spectrometers, sensors and also benches for generating gas or liquid samples, the Analysis team carries out feasibility studies and matches the industrial needs and innovative solutions of technology providers. All the data presented below were obtained with a GC-FID piloted by the Axel'One team.

The main goal of these tests was to generate, from a single solution, standards of gaseous hydrocarbons at different concentrations and then to characterize them using a GC-FID equipped with a gas injection valve. The system used is schematized below:

Generation of standards from a mixture of hydrocarbons with LiqMix™ Cascade

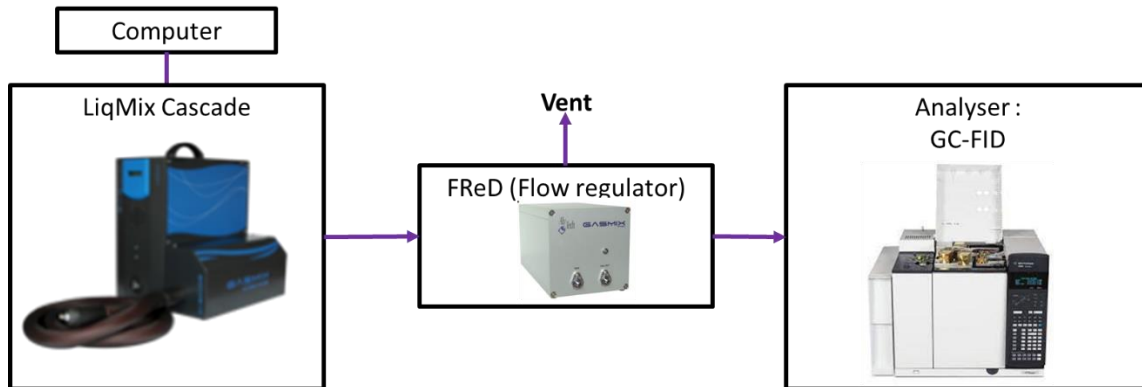


Figure 1: Schematic of the calibration system.

For these tests, the hydrocarbon concentration ranges varied from 100 ppm (mol) to 7 ppm (mol). A sequence created on the LiqMix™ Cascade software made it possible to program the generation of different concentration levels (figure 3). Each stage was calculated from a requested Hexane concentration, the concentration of the other hydrocarbons of the initial mixture was recalculated automatically by the software. All this information can be generated in a report as shown in Figures 4 and 5:



Figure 1: LiqMix™ Cascade Software

Sequence	Hydrocarbons	Air/N2	Decane	Hexane	Octane
# 3/6	1,502 g	2031,695 N	47,291 +/-0,765	40,000 +/-1,121	31,768 +/-0,890
# 4/6	1,502 g	2031,695 N	40,936 +/-1,131	60,000 +/-1,658	47,652 +/-1,317
# 5/6	1,502 g	2031,695 N	54,581 +/-1,489	80,000 +/-2,182	63,536 +/-1,733
# 6/6	1,502 g	2031,695 N	68,227 +/-1,838	100,000 +/-2,694	79,421 +/-2,140

Figure 3: Sequence preparation on the software.

Generation of standards from a mixture of hydrocarbons with LiqMix™ Cascade



Synthèse de Projet

Date : 21/01/2022 09:37
 Utilisateur : NoUser
 GasMix S/N : L18-146C
 Révision logicielle : 118

Nom du projet : hydrocarbures ppm (1.5ml min)_211022_104310

Configuration de l'Instrument

	Voie n°1	Voie n°2	Sortie 1er étage	Dilution 2ème étage
Etalon	HYDROCARBURES	Air/N2	Air	Air/N2
Débit mini	0,109 g/h	200,0 Nml/min	1,179 Nml/min	100,458 Nml/min
Débit maxi	4,99 g/h	5141,795 Nml/min	49,89 Nml/min	5146,49 Nml/min
Analytes	HEXANE 40,38 % OCTANE 32,07 % DECANE 27,55 %			

Voies chauffées (°C)

LINE	OUTLET	Evaporator
60	60	60

Figure 4: Instrument configuration report example.



Synthèse de Projet

Récapitulatif de la séquence

Mélange 1 / 6 :

Description

Pause avant	Injection	Pause après	Cycle	Répétitions	Durée totale
00:00:00	01:05:00	00:00:00	01:05:00	1	01:05:00

Relais

	1E	2E	1I	2I
ON	---	---	---	---
OFF	---	---	---	---

Analytes

	DECANE	HEXANE	OCTANE
Concentration	6,823 ppm	10,000 ppm	7,942 ppm
Incertitude	+/- 0,244 (abs.)	+/- 0,358 (abs.)	+/- 0,284 (abs.)

Débites

Voie n°1	Voie n°2	Sortie 1er étage	Dilution 2ème étage
1,502 g/h	2031,7 Nml/min	1,2 Nml/min	119,5 Nml/min

Débit total : 120,7 Nml/min

Figure 5: Mixture creation report.

For this application, the concentration levels are as follows:

- o 100, 80, 60, 40, 20, 10 ppm(mol) for Hexane.
- o 79, 64, 48, 32, 16, 8 ppm(mol) for Octane.
- o 68, 55, 41, 27, 14, 7 ppm(mol) for Decane.

Each stage has a fixed duration of approximately 1 hour and the transition between stages is carried out automatically by the software.

The absolute uncertainty of the hydrocarbon concentrations is calculated by the algorithm developed by AlyTech and displayed in the LiqMix™ Cascade software. For this experiment and under these conditions, the relative generation uncertainty is $\pm 3.5\%$ for all the mixtures.



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LiqMix™ Cascade results by GC-FID

The GC-FID parameters have been optimized for calibration in hydrocarbons following Axel'One's recommendations. Here are the instrument settings and the column used:

Agilent 7890B GC-FID parameters :			
Temperature	Inlet	Detector	Column
Setpoint : 35°C	Mode : Splitless	FID	DB1
Hold Time : 2min	Temp : 240°C	Makeup : N2	Model : 125-10HB
Post Run : 35°C	Gaz Valve : 250µL	H2 Flow : 35 mL/min	Diameter : 530.00µm
#1 Rate : 20°C/min		Air Flow : 450 mL/min	Film thickness: 2.65µm
#1 Value : 90°C		Temp : 250°C	Length : 10.0m
#1 Hold Time : 0.5min			Void time : 0.179min

Table 2: Parameters of the GC-FID method

In this configuration, a sequence with levels of hydrocarbon concentrations was generated:

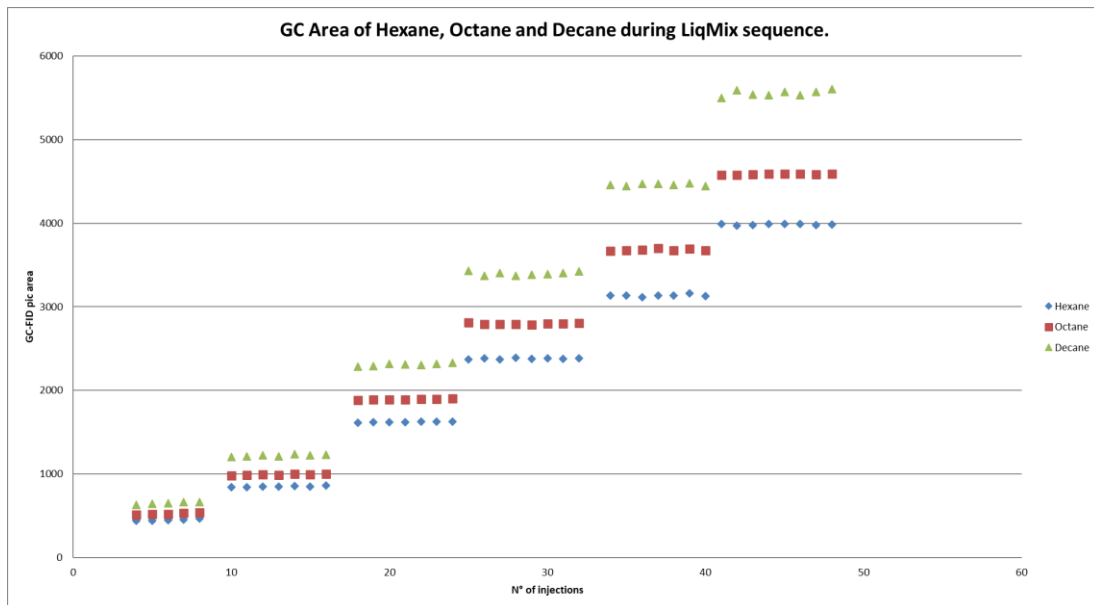


Figure 6: Integrations of GC-FID hydrocarbon peaks during the LiqMix Cascade sequence

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The areas of the hydrocarbon peaks are integrated then compiled in the following table:

Concentration (ppm mol)	Average (Area)	Standard deviation (Area GC-FID)	RSD %
Hexane			
100	3984	10	0,2
80	3135	13	0,4
60	2380	7	0,3
40	1621	5	0,3
20	850	6	0,8
10	450	10	2,2
Octane			
79	4469	5	0,1
64	3681	11	0,3
48	2797	8	0,3
32	1891	7	0,4
16	991	8	0,8
8	524	11	2,1
Decane			
68	5555	35	0,6
55	4460	13	0,3
41	3397	22	0,7
27	2308	15	0,7
14	1221	12	1,0
7	652	14	2,1

Table 3: Compilation of data obtained during hydrocarbon analysis by GC-FID

Table 3 shows good RSDs (<5%) over the entire range.

In a single sequence, these data made it possible to establish the calibration lines for each compound of the hydrocarbon mixture:

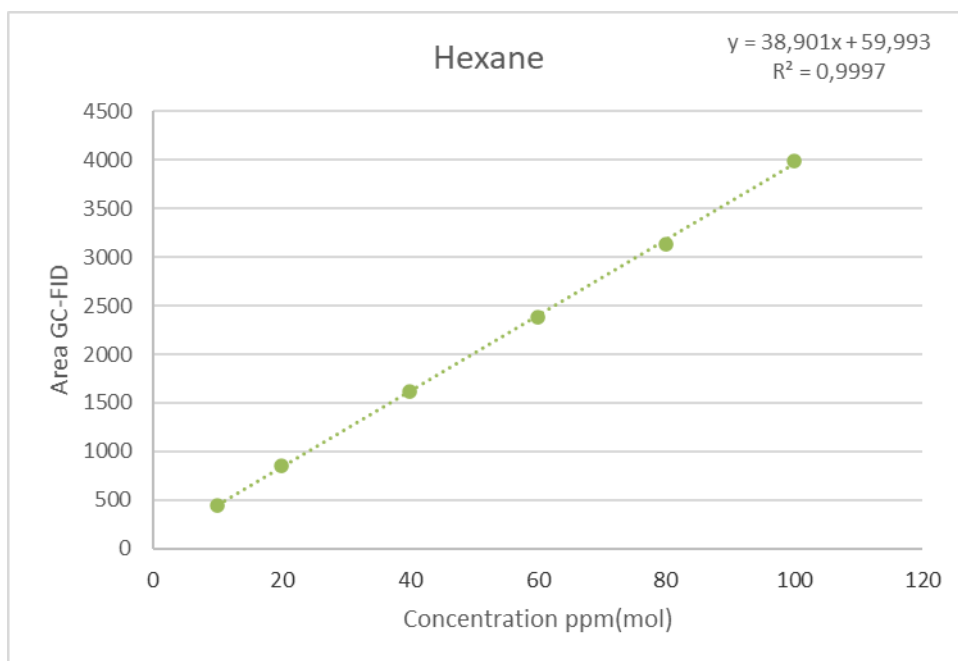


Figure 7: Hexane calibration curve.

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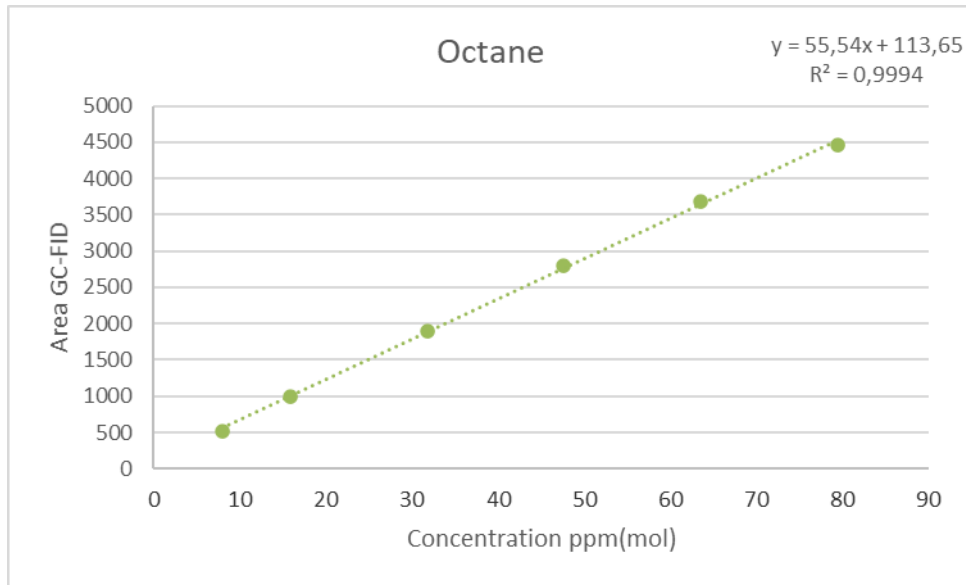


Figure 2 : Octane calibration curve.

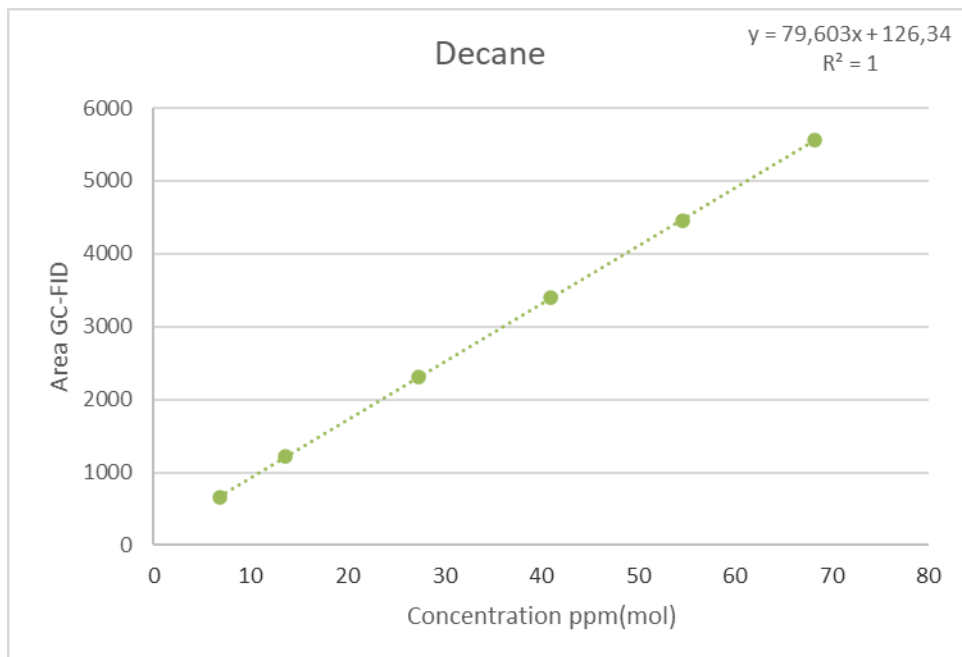


Figure 3: Decane calibration curve.

With the study of these calibration lines, good linearity was observed for each compound: $R^2 = 1$, $R^2 = 0.9997$, $R^2 = 0.9995$. Linearity has therefore been validated over the range from 10 to 100ppm (mol) for Hexane, from 8 to 79ppm (mol) for Octane and 7 to 68ppm (mol) for Decane.

Conclusion

With AlyTech's LiqMix™ Cascade system, this study demonstrated that the generation of standard gases from a mixture of hydrocarbons is possible in a faithful and accurate manner. The available concentration range depends on the configuration of the diluter flowmeters. As part of these tests, a range of 7 to 100ppm mol has been generated and the average associated uncertainty is $\pm 3.5\%$ relative.

LiqMix™ Cascade is versatile and shows very good linearity, within the dynamic range of GC-FID. The generation of standards from a single mixture makes it possible to obtain several calibration lines quickly and reliably in a single analysis sequence.