# Controlled humidity generation with LiqMix ™

## LiqMix™, a gas standard diluter

Some applications require gas standards that are not available in cylinders, or your needs for a specific gas mixture vary frequently and you need them quickly in varying concentrations.
The LiqMix™ diluter, developed by AlyTech, produces these custom calibration gases from pure liquids or mixtures by vaporizing the liquid phase in a gas stream, with the possibility of adding other gases to this mixture.

LiqMix™ is a simple and efficient tool for performing multi-point 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 to work with mixtures such as BTEX, other volatile hydrocarbons, siloxanes, water, ethanol, or any other organic compound.

## Controlled humidity generation

One of the typical applications is the generation of controlled humidity. Depending on the configuration of the LiqMix™ the absolute water concentration can range from ppb (mol) to % (mol). To do this, the liquid channel must be supplied with "general laboratory water" quality water, i.e. category 2 water according to the ISO 3696: 1995 standard. The gaseous channel is supplied with a pure gas very limited in water. The required inlet pressures for liquid and gas depend on the configuration of the LiqMix™ and generally vary between 3 and 5bar(g). The LiqMix™ outlet is usually at atmospheric pressure, but it can also deliver the gas with a pressure of 1 or 2 bar(g) if necessary.

The various elements of the LiqMix™ are thermo regulated to vaporize and maintain water in the vapor phase according to the desired levels and the outlet pressure. The table below shows the setpoint temperatures for the example of humidity generation presented in the following chapter.

| Components | Temperature (µGC Config) | Temperature (Raman Config) |
|---|---|---|
| Vaporizer | 80°C | 107°C |
| Mixing chamber | 90°C | 117°C |
| Transfer line | 90°C | 117°C |

Once the sequence has been configured and started, the desired mixture (s) are obtained at the outlet of LiqMix™.

## Example of humidity generation with LiqMix™

The data presented below was obtained by Axel'One. Axel'One collaborative innovation platform was created in 2011 near Lyon with the main missions of pooling services, tools and skills to support projects in chemistry and the environment. The platform also offers R&D services thanks to a wide range of research and scale-up tools.

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.

The main goal of these tests was to humidify, using a LiqMix™, a nitrogen flow in order to create gaseous standards at different concentrations of water and then to characterize them using a Raman spectrometer as well as a micro-GC (Figure 1).

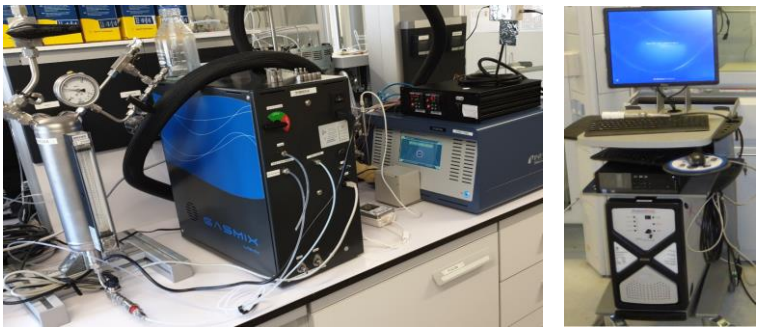

*Figure 1: Picture of the set up at Axel'One's laboratory*

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For these tests, the water concentration range varied from 0.5% (mol) to 20% (mol). The measurements are expressed in absolute and not relative humidity.
A sequence was created on the LiqMix™ software, which made it possible to program the generation of different concentration levels as shown in Figure 2:

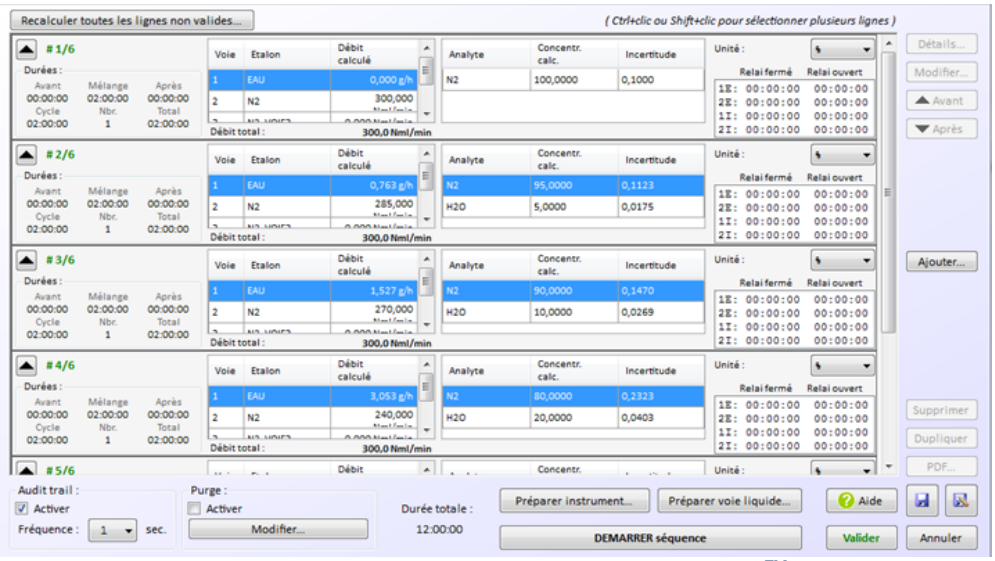


*Figure 2: Sequence lines prepared in the software LiqMix™*

For this application, the concentration levels generated were as follows: 0, 0.5, 1, 5, 7.5, 10, 20 (%mol).
Each stage has a fixed duration of 2 hours and switching between stages is automatic.
The relative uncertainty of the water concentrations for each stage was calculated and displayed in the LiqMix™ software by the algorithm developed by AlyTech. For this experiment and under these conditions, the relative generation uncertainty varied between ±0.01% and ±0.07%.

## LiqMix™ results by Raman

The device used was the Raman KAISER 532 nm with the AirHead gas probe.
The output of the LiqMix™ to the Raman probe was pressurized to 1.5 bar(g) to be able to carry out these analyses.
The analyses were performed with an integration time of 10 sec - 12 scans, which makes 120 seconds per spectrum in total.
The reprocessing of these spectra makes it possible to determine the calibration curve and the associated measurement error (figure 4):

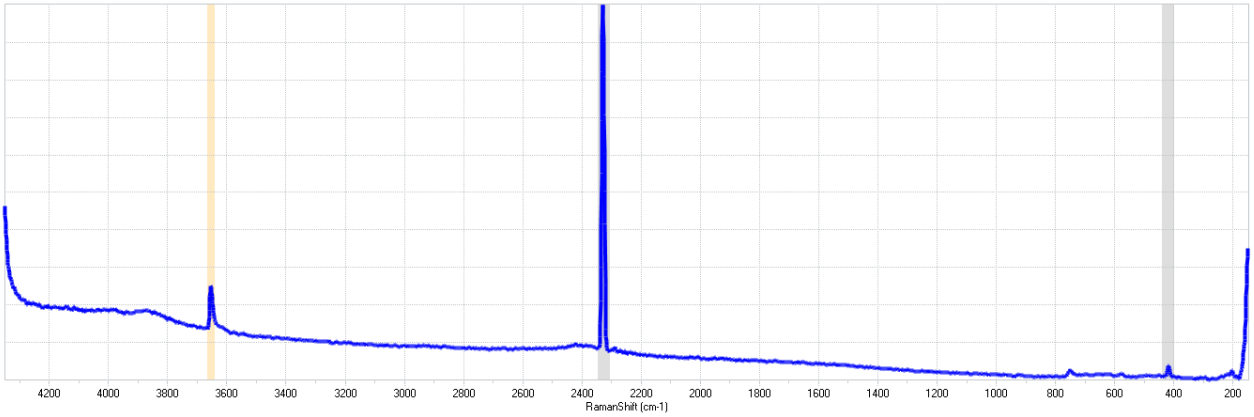


*Figure 2 : Example of Raman spectrum obtained with LiqMix™ for a humidified nitrogen flow; the characteristic bands of water and $N_2$ are at 3683 $cm^{-1}$ and at 2330 $cm^{-1}$*

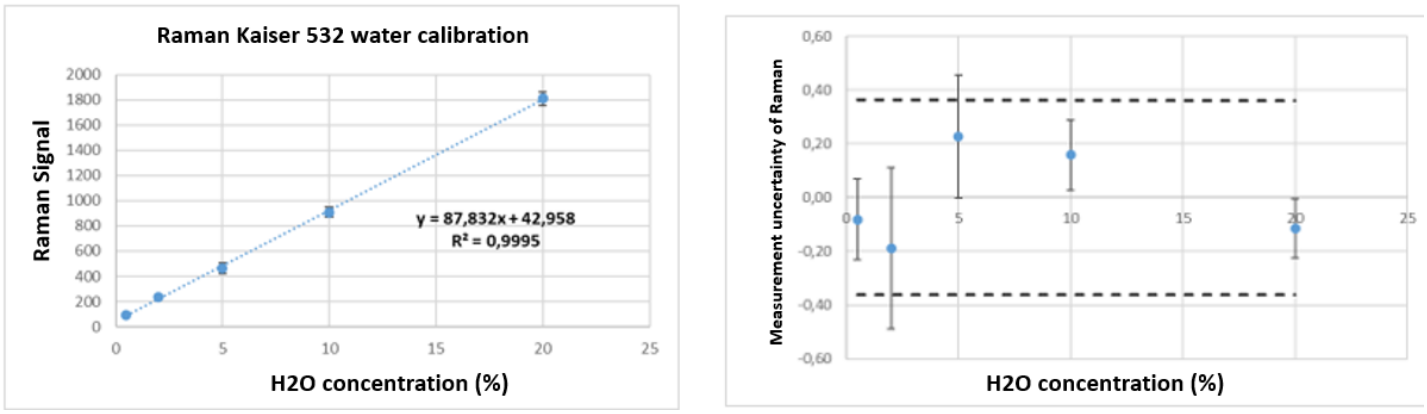


*Figure 4: Raman calibration curve and associated measured absolute error*

The water quantification using Raman Kaiser 532 nm spectrometer is achievable in these contents of 0.5 to 20 mol%, with an $R^2$ of 0.999 and an average absolute error of ± 0.36%.

## LiqMix™ results by µGC

The µGC used was the INFICON FUSION equipped with three modules with TCD detector: Sieve 5A, RTQ and Stabilwax. For this study, the peak water was observed on the Stabilwax module.

| Parameters | Module A Sieve 5A | Module C Stabilwax |
|---|---|---|
| Sample inlet Heater (°C) | 100 | 100 |
| Time Sample pump (s) | 20 | 15 |
| Inject Time (ms)<br>Backflush Times (s) | 0<br>10 | 10 |
| Injector heater (°C) | 100 | 100 |
| Column pressure (psi) | 30 | 25 |
| Column temperature profile (°C) | 90 | 110 |
| Detector TCD frequence (Hz) | 50 | 50 |

*Figure 5: Parameters of the method used for water analysis on the micro-GC*

At the inlet of the µGC, a filter which retains the liquid particles named “genie filter” was installed and heated between 70°C and 80°C by a heating wire. In this configuration, the chromatograms obtained are shown in Figure 6:

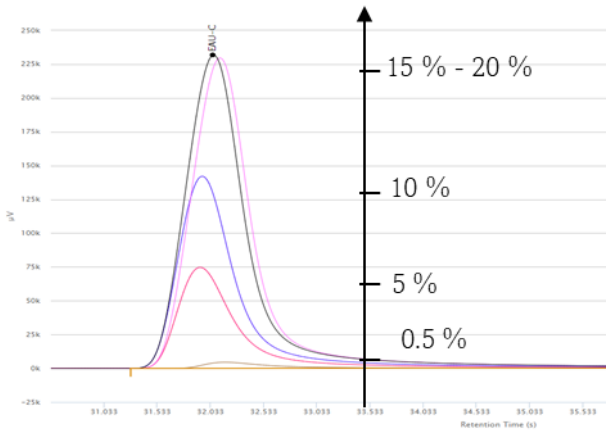


*Figure 6: Water chromatograms obtained on the Stabilwax module*

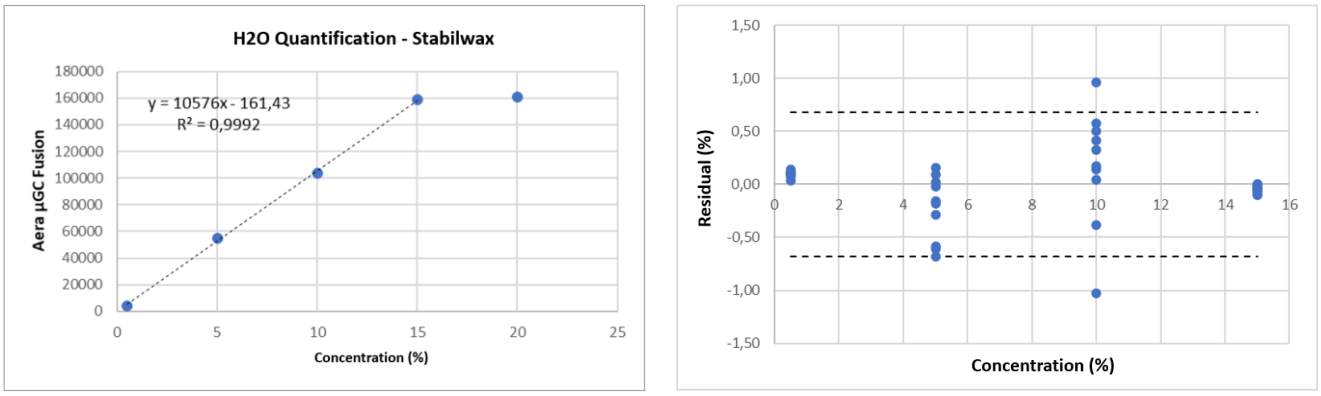


*Figure 7: Water calibration curve (0.5 - 15%) and associated uncertainty (± 0.67%)*

Figure 7 shows a good linearity ($R^2$ = 0.9992) with the Stabilwax module for a range of 0.5 to 15% mol humidity. The nonlinear response profile when the 20% is included is due to the µGC. This was confirmed by the fact that the results on the Raman were linear.

This range could be extended by optimizing the µGC analysis method by adjusting the injection volumes. LiqMix™ allows to evaluate the linearity range of water in different µGC configurations.

## Conclusion

With LiqMix™, this study carried out by Axel'One has demonstrated that the generation of humidity is possible in a faithful and accurate manner on two different analytical systems. The range depends on the configuration of the diluter flowmeters. In these tests, a range of 0.5 to 20% mol was generated and the study of the measurement uncertainties on the flowmeters showed high precision on the concentration, respectively ± 0.01 to 0.07% soft. The analysers are responsible for most of the associated measurement uncertainty.

LiqMix™ is versatile and shows very good linearity, confirmed by Raman and µGC analyses, in the dynamic range of the analysers.