METHOD DEVELOPMENT FOR THE ANALYSIS OF C1-C5 HYDROCARBONS IN FUEL CELL HYDROGEN WITH CALIBRATION GAS GENERATED FROM STANDARD GAS AND LIQUIDS

The controlled introduction of liquid compound in gas mixtures is not a trivial analytical task and it was earlier only achievable by a permeation tube and old style static dilution techniques. Recently developed by AlyTech, the automated LiqMix Cascade system however introduces liquid into a gas stream at different concentrations in a simple and reliable way to perform multi-point calibrations, linearity and detection limit checks. This article describes an example of its use for LOQ / LOD validation of an analytical method GC-Precon-PDHID.

Introduction

To perform multi-point calibration, linearity checks, LOQ/LOD validation laboratories have to keep significant stock of the standard gas cylinders with various concentrations. Gas calibration standards are expensive to order, delivery times are long and validity of the certificate is relatively short. To save money and gain flexibility, many laboratories use dynamic gas mixers. With precise gas mixers/ diluters the calibration gas is easy to generate on site at the desired concentrations, even to very low levels. This practical solution is easy to put in place for gas standards available in the cylinders.

An issue may arise when some chemicals are not found in commercially available cylinders, like unstable, reactive compounds, or when it is a liquid. The introduction of the high boiling point compounds in gas mixtures was once only achievable with a permeation tube and old style static dilution techniques. Recently developed by AlyTech, the LiqMix Cascade system introduces liquid into a gas stream in a simple and reliable way.

Generate gas standard from a liquid

The LiqMix Cascade is an accurate calibration tool designed for automated generation of customised standard gas from neat liquids or liquid cocktail mixtures for the purpose of calibrating gas analysers, GC or GC/MS, and to validate the precision and reliability of GC sample introduction systems. Due to its unique intelligent multi-stage cascade dilution, AlyTech LiqMix Cascade can provide a very wide range of concentrations from % down to ppb levels with good accuracy, high repeatability and full traceability. Gas standards such as BTEX in air, other hydrocarbons, siloxanes, ethanol and phenol, humidity standards can be delivered.

All interconnections and outlet line of LiqMix are heated in order to maintain the vapours in gas phase and thus avoiding re-condensation up to the delivery point.

Easy to handle, dedicated AlyTech software controls the operation, manages mass flow controllers, its calibration tables, performs automatic calculation of liquid and span gas flows, to achieve desired concentration of analytes even for very complex multicomponent mixtures. Following highest metrology requirements the instrument not only accurately prepares the gas mixtures, but it also automatically calculates and reports maximum relative uncertainty for every delivered concentration.

Rich remote control functionalities of the software and automated programmed sequences enable full automation by synchronising the mixer/diluter with a gas chromatograph, pre-concentrator, spectrometer, gas analyser or other system.

LiqMix Cascade

Investigation of common hydrocarbon contaminants in hydrogen fuel

Recently the AlyTech LiqMix Cascade was successfully used for validation of analytical methods to assess the purity of automotive fuel cell grade hydrogen. Impurities commonly found in hydrogen gas for fuel cell vehicles may have some disastrous long-term consequences on the fuel cells if their levels exceed 2 ppm. Appropriate analytical methods must be able to function in a hydrogen matrix, and detect and quantify regulated by ISO 14687-2 contaminants present at ppmv–ppbv concentrations. In the framework project called Metrology for Hydrogen Vehicles (MetroHyVe) funded by European Metrology Programme for Innovation and Research (EMPIR) AlyTech instrumentation was employed at Institute for Energy Technology (IFE) - one of the most experienced petroleum gas and research laboratories in Norway. The specific focus of IFE was on common hydrocarbon contaminants in hydrogen fuel that ranged from polar components - methanol, ethanol and acetone, to non-polar components - methane, ethane, propane, butanes, pentanes. The large span in boiling points and polarity of the analytes make the target matrix challenging to create in laboratory conditions and introducing it into pure hydrogen and analyse. This challenge was overcome by using the LiqMix Cascade to generate homogeneous mixture of hydrocarbons (see Table 1) and introduce sub-ppm impurities in pure hydrogen 5.0 gas. Working range of concentrations for hydrocarbons mixture was 0.2 – 20 ppm.

Table 1 Mix of hydrocarbons used in the study

	Compound	Analytical Method	Span / ppb
Gas	C2	GC-Precon-PHID	200 3500 6800 10100 13400 16700 20000
	C3	GC-Precon-PHID	
	C4's	GC-Precon-PHID	
Liquid	C5's	GC-Precon-PHID	
	C6	GC-Precon-PHID	
	MeOH	GC-Precon-PHID	
	Acetone	GC-Precon-PHID	
	EtOH	GC-Precon-PHID	

The analytical setup

Linearity and detection limit were determined using the standard mix at different concentrations generated by LiqMix Cascade from liquids and gas, with 2 stages of dynamic dilution.

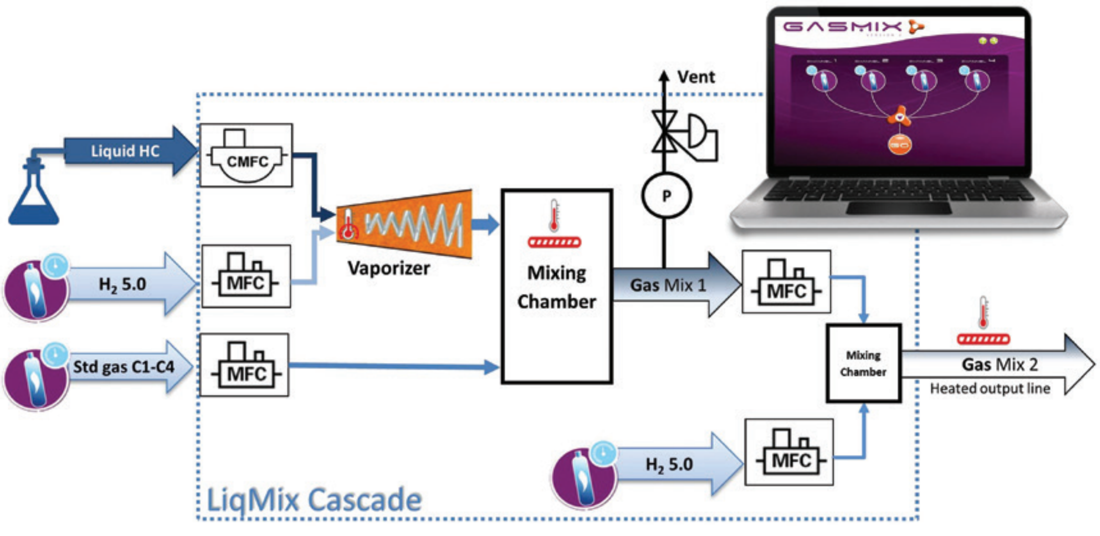

Figure 1. LiqMix Cascade schematics

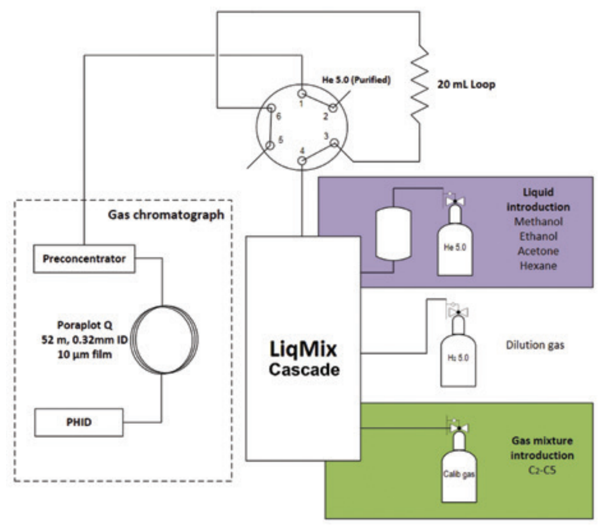

Figure 2. Schematics of GC-Precon-PHID and standard gas generator

The liquid components were tared in advance using a laboratory balance, loaded in the reservoir and pressurised with helium 5.0. With its Coriolis mass flow controller LiqMix Cascade accurately delivered the liquid hydrocarbon mixture into a vapouriser where it evaporated into a flow of a carrier gas (hydrogen 5.0). In a gas phase, it was transferred to a mixing chamber where it was later mixed with a second stream of calibration gas C1-C4 (Praxair standard gas mixture) introduced into the mixing chamber by an accurate thermal mass flow controller.

To achieve very low concentrations a portion of homogenous gas/vapour mixture is delivered to the second dilution stage, so-called Cascade, where it is further diluted by a stream of pure hydrogen and transferred to a sampling point by heated line.

Picture 2. Photo of installation

Optimisation of cold trap using GC-Pre-concentration-PDHID

The cold trap was a key performance component in the study on fuel hydrogen impurities and was examined by using a separate GC-system with PHID detector.

Standard gas mixtures were prepared in the same way as described above by LiqMix Cascade. The samples were introduced through a heated (70 degrees Celsius) 20 mL sulfinert gas loop for 6,5 minutes. 30 seconds was allowed for the gas pressure to stabilise before the loop was emptied through sulfinert tubing, using purified helium 5.0, into a PTV-injector. The PTV temperature held -10°C by use of liquid nitrogen.

After 6 minutes of purging the loop the PTV temperature was increased 5 °C/min until reaching the end temperature of 110°C. The content of the cold trap was focused on a Varian Poraplot Q column (52m, 0.32mm ID, 10 micrometer) at -10°C with helium carrier at constant flow.

The oven was kept at -10°C for 15 minutes to separate air and methane and then ramped to 170°C at10°C/min rate. The compounds were detected by use of Photo Discharge Helium Ionisation Detector (VICI PDHID for Agilent 7890A). One of chromatograms is presented on the Figure 3.

Uncertainty and standard deviation associated with lowest achievable concentrations of analytes in this study are presented in the Table2. Initial concentrations of components were approximately 0.1% mol/mol.

In the worst case of operation at maximum dilution ratio and lowest concentration, the LiqMix Cascade system did show the reasonable relative error at about 3% for gas standards from

Table 2 Uncertainty and standard deviation associated with lowest achievable concentrations by Liqmix Cascade.

Analyte	Concentration, ppb-mol	Liqmix Uncertainty, ppb	RSD % Liqmix
1-Pentene	0,981	0,057	5,810
1-Butene	1,019	0,057	5,594
Ethylene	3,000	0,127	4,233
Isopentane	3,846	0,164	4,264
Neopentane	3,904	0,166	4,252
Pentane	3,913	0,166	4,242
Propene	4,798	0,205	4,273
Isobutane	9,808	0,415	4,231
Butane	9,808	0,300	3,059
Propane	12,500	0,456	3,648
Ethanol	13,396	0,445	3,322
Methanol	15,094	0,491	3,253
Ethane	19,615	0,721	3,676
Acetone	20,010	0,630	3,150

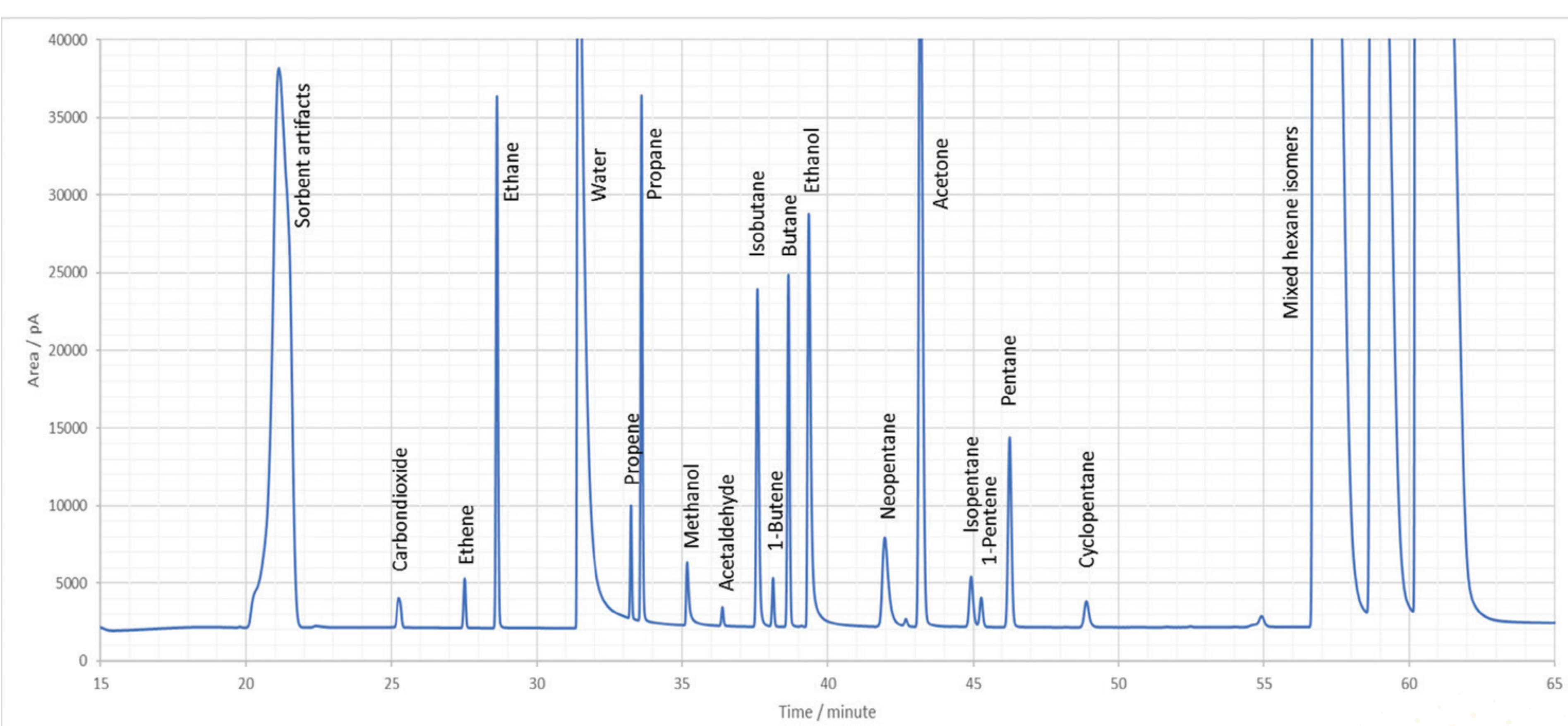

Figure 3. Chromatogram GC-Preconcentration-PHID.

Table 3 Lower Limit of Detection and Lower Limit of quantification using sub-ambient preconcenration (-10 degrees Celsius) and sorbents on GC with photon discharge helium ionisation detector (PHID) using standard mixtures generated by Alytech LiqMix Cascade

Analyte	LOD n=10, 3σ), ppb-mol	LOQ (n=10, 10σ), ppb-mol
1-Pentene	0,230	0,767
1-Butene	0,169	0,562
Ethylene	0,584	1,946
Isopentane	0,783	2,611
Neopentane	0,626	2,087
Pentane	0,600	1,999
Propene	1,054	3,512
Isobutane	1,512	5,039
Butane	1,615	5,382
Propane	2,189	7,297
Ethanol	4,143	13,809
Methanol	4,650	15,499
Ethane	3,424	11,413
Acetone	5,915	19,716

liquids and good linearity in the range of 15 ppb to 20 ppm.

Lower limit of quantification (LOQ) and lower limit of detection (LOD) were calculated using repeated injections of the lowest standard (n=10). A response factor was calculated using the average area and the amount. The response factor was applied to the standard deviation and the LOD and LOQ was calculated by using 3 standard deviations and 10 standard deviations (see Table 3).

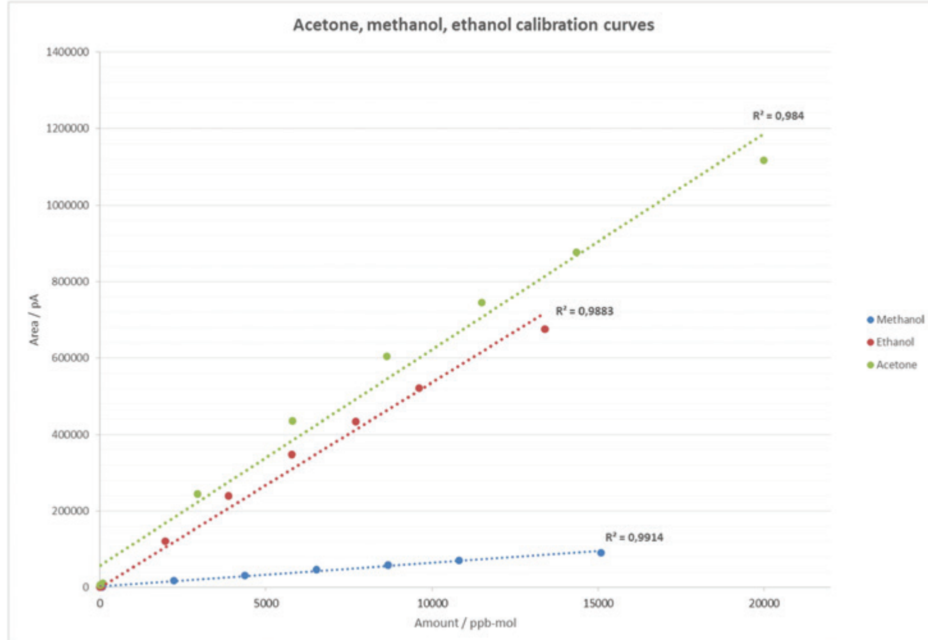

Figure 4 Linearity of generated concentrations

Conclusion

Alytech LiqMix Cascade was found to be a very valuable tool when it is required to generate a gas standard in wide concentration range from complex chemical mixtures, including liquids. The system dramatically accelerated the research work, reduced labour time of analytical chemists and saved a considerable amount of money by producing on-site hydrocarbons calibration gas mixtures down to ppb levels accurately and with high repeatability. Flexibility of the system and its GasMix software fit well to different analytical techniques and serve for linearity check, multipoint calibration, LOQ and LOD determination, and other analytical needs.

References Cited

1. ISO 14687-2 - Hydrogen fuel - Product specification - Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles, 2012, International Organization for Standardization

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