XIX IMEKO World Congress
Fundamental and Applied Metrology
September 6–11, 2009, Lisbon, Portugal

ETHANOL PRIMARY GAS STANDARDS PREPARATION

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Abstract – In this paper it will be discussed the gravimetric method to produce ethanol primary gas standards according to the international standard ISO6142 [1].

The ethanol gas standards are prepared by vaporizing ethanol in nitrogen and compressing them in a pressurized cylinder. During the preparation process careful control of weighing and all parameters that can influence it, such as air temperature, pressure and humidity, shall be made.

The standards composition are further analysed by the analytical method non dispersive infrared spectroscopy (NDIR). The traceability is assured comparing the composition with national standards of mass, pressure, temperature and other national/international amount of substance standards.

Keywords: ethanol, gas, standards

1. INTRODUCTION

The Portuguese NMi (LCM) of the Portuguese Institute for Quality (IPQ) is the primary laboratory for the SI base quantity amount of substance. It is also the national entity for the metrological control of evidential breath analysers, used by the authorities to enforce driving under the influence of alcohol laws. One of its concerns is to have accurate ethanol standards that can provide accurate, reliable and traceable breath tests. Traceability to SI units ensures that the results obtained from breath analysis are accepted as evidence.

For the metrological control of evidential breath analysers different methods are accepted by the scientific and metrology community, namely, dry compressed ethanol gas mixtures and wet breath alcohol simulators. The first one, which production method will be here discussed, is each time more used by the metrology national authorities.

In the 90's Dubowski [2] and Silverman [3], independently, tested and compared both systems having concluded that both practices are feasible, valid and equivalent. While in wet simulators the devices simulate ethanol vapour in human health, which includes O_2, CO_2 and water composition, as well as, breath temperature, in the ethanol gas mixtures it is only used the ethanol molecule in a matrix of nitrogen or air, which turn it easier to produce and manipulate for its purposes.

Several ways are known for introducing accurate amounts of ethanol into a pressurized cylinder. It can be through the use of micro syringes, small containers or even with micro-injectors [4]. However this article will focus on the syringe method.

2. EXPERIMENTAL

2.1. Mixture feasibility

The first step when preparing an ethanol gas mixture is to check the feasibility of the mixture regarding some limitations, namely, chemical reactions with the materials and condensation of ethanol vapour to a liquid phase.

Despite that ethanol is not highly reactive it must be only chosen materials (cylinder, valve and seals) which are inert to ethanol or other components in the mixture. A passivation treatment reduces the adsorption/desorption phenomena on the cylinder internal walls improving ethanol stabilisation.

Concerning condensation, as ethanol is a liquid at PTN conditions it can easily liquefy if care is not given to the subject. Therefore "*…the filling pressure shall be set safely below the dew-point vapour pressure of the final mixture at the filling temperature*." [1] The same care shall be taken during storage and filling

The estimation of filling pressure limits can be previewed by the following approximation: [1]

$$p_F = \frac{P_V^T}{x_e} \qquad (1)$$

p_F : maximum filling pressure;

x_e : mole fraction of ethanol;

P_V^T : ethanol vapour pressure at temperature T;

For a safe use of the standards at temperatures down to 8 ºC, the cylinder can be filled up to 10 MPa, for ethanol in nitrogen compositions up to 160 µmol/mol.

For higher concentrations the filling pressure shall be lower. Higher than 750 µmol/mol it is not worth to produce a pressurized ethanol mixture since its maximum filling pressure will be lower than 3,5 MPa, considering the ethanol vapour pressure at 8 ºC (P_v = 2,63 kPa) [5].

2.2. Purity analysis

Purity analysis of both ethanol and nitrogen is a critical factor regarding the standards accuracy produced. Actually the impurities in the parent gases are the main contributors for the final uncertainty. The ethanol used is 99,8 % (mol/mol) pure and the nitrogen is 99,99990 % (mol/mol) pure. These specified values are checked and reanalysed with analytical techniques such as gas chromatography (GC) and Fourier transform infrared spectroscopy (FTIR).

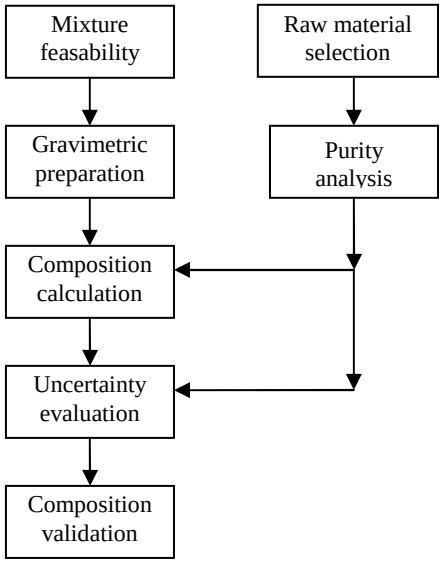

Fig. 1. Preparation generic scheme [9]

2.3. Gravimetric preparation method

Prior to the preparation, the cylinder must be cleaned and evacuated in a vacuum station. After reaching a vacuum of magnitude of 10 µPa, the cylinder is ready to be filled.

The filling is performed in a sequence of steps summarised below:

-the empty cylinder is weighed in a mass comparator, where it is compared against a cylinder with identical volume and shape;

-the syringe is weighed empty and filled with the desired amount;

-the evacuated cylinder is connected to the filling station with a pressurized nitrogen cylinder connected upstream;

-the syringe is unloaded to the filling station and afterwards the pure nitrogen will flow through the system causing the ethanol evaporation and forcing it to the cylinder;

-after filling both the filled cylinder and the empty syringe are weighed again;

-finally the mixture is rolled for homogenisation and stabilisation purposes.

2.4. Uncertainty evaluation

Regarding this preparation procedure three categories of uncertainties sources can be found, namely, the weighing process, the ethanol and nitrogen purity, and the molar masses[1].

The weighing uncertainties sources are mainly from the balance (resolution, drift, cylinder location on the pan), weights (used on the comparator), the buoyancy effects (due to atmospheric density changes) and the residual gas (cylinder purging).

The raw materials used are not 100% pure. Therefore their impurities content have an uncertainty. Even if there is an impurities specification from the supplier, the laboratory makes its own purity analysis for checking and validation.

The molar masses values are determined from the atomic weights and associated uncertainties from IUPAC.

Other sources such as the surface treatment can cause adsorption/desorption reaction causing the mixture destabilisation.

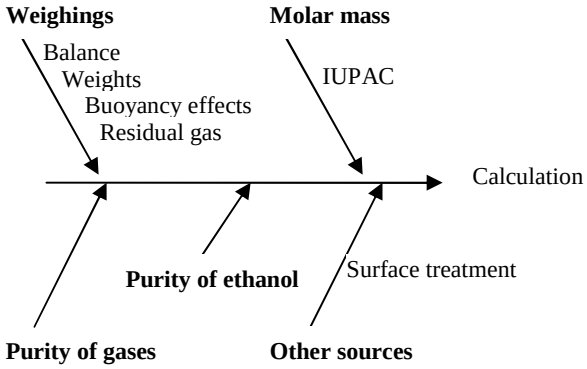

Fig. 2. Uncertainty diagram

2.4. Composition validation

Once the mixture is finished the final composition can be calculated and expressed as mole fraction (mol/mol). As the mole fractions of ethanol used as standards materials are considerably low, it is usual to express in µmol/mol (ppm). Expressing the composition in mole fraction makes it independent from pressure or temperature changes.

Finally, after composition determination, the value is validated by comparing it with other primary ethanol gas standards in accordance with the ISO6143 standard. The analytical method used is the NDIR spectroscopy.

The validation criterion is:

$$\left|x_{grav} - x_{anal}\right| \leq 2\sqrt{u\left(x_{grav}\right)^2 + u\left(x_{anal}\right)^2} \qquad (2)$$

Where x_{grav} and x_{anal} are the gravimetrically and analytically measured mole fraction and $u(x_{grav})$ and $u(x_{anal})$ are the correspondent uncertainties.

Our calibration measurement capability (CMC) for the ethanol mixtures in nitrogen is (100 – 500) µmol/mol with an associated relative expanded uncertainty between 0,7 % and 1,6 %. IPQ demonstrated it through the participation in the comparison CCQM-K4 “Ethanol mixtures in nitrogen” conducted by the Consultative Committee for Amount of Substance of BIPM [7]. Therefore its CMC are recognized

by all participants of the Mutual Recognition Arrangement (MRA) drawn up by the CIPM.

4. CONCLUSIONS

The gravimetric method for the preparation of primary ethanol gas standards was presented being a primary method for the production of accurate and reliable standards. It allows to directly link the gas standards to national standards of mass, temperature and pressure, and, through the IUPAC molar mass definition to the base quantity amount of substance. It is, therefore, assured the traceability to the International System of Units (SI).

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