SHORT REPORT

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J. Chem. Metrol. 19:2 (2025) 260-264

journal of chemical metrology

Desorption of ethanol from internal surface of the cylinders

Luděk Král [1,2*], Jiří Tesař [1,2] and Miroslav Bárta [1]

[1] *Czech metrology Institute, Okružní 31, 638 00 Brno Czech Republic*
[2] *Slovak University of Technology in Bratislava, Faculty of Mechanical Engineering, Nám. slobody 17, 812 31 Bratislava Slovakia*

(Received July 30, 2025; Revised October 14, 2025; Accepted October 15, 2025)

Abstract: Reference materials (RMs) are essential for ensuring metrological traceability in various fields, including environmental monitoring, chemical analysis, and the verification of alcohol breath analyzers. One critical property of RMs is their long-term stability, particularly for gas mixtures such as ethanol in nitrogen, which are stored in pressurized aluminum cylinders. This paper describes the preparation of such gas mixtures according to ISO 6142-1, utilizing differential weighing to minimize the influence of ambient conditions and ensure accurate composition. The effects of adsorption of ethanol on the internal surfaces of aluminum cylinders were experimentally investigated. Results indicate that ethanol can remain adsorbed on the cylinder walls even after evacuation, leading to measurable ethanol concentrations upon subsequent refilling with nitrogen. Repeated fillings demonstrated a decrease in ethanol levels, confirming the saturation and gradual desorption behavior. These findings underscore the necessity to consider adsorption effects in the uncertainty budget and composition calculations for low-concentration ethanol-in-nitrogen RMs.

Keywords: Stability; reference materials; ethanol; pressurized cylinder; gas chromatography; desorption.

1. Sample Source

All samples used in this study were prepared in CMI's laboratory, accredited as a certified reference material producer according to ISO 17034:2016 [1].

2. Previous Studies

Reference materials (RM) are one basic part of the metrological traceability. They are used in many necessary fields of measurement. Calibration of detectors for monitoring the environment, in chemistry analysis, and alcohol breath analysers verification are example of usage of reference materials. One of the most essential properties of every RM is long-term stability.

Ethanol in nitrogen RM, in gaseous form, is used for the alcohol breath analyser. This RM is prepared for pressurized cylinders and assesses its long-term stability over one year [2]. Not only the composition of the prepared RM could influence the stability. The internal surface of the used cylinder also determines the stability of RM. In the case of ethanol in nitrogen prepared in a cylinder with an aluminium surface, there is a small amount of ethanol adsorbed on the surface of the cylinder.

Especially in connection with oxygenated volatile organic components (VOCs), there are possibilities of adsorption to surfaces. VOCs are defined as a group of organic chemicals that easily

* Corresponding author e-mail: ludek.kral@cmi.gov.cz, +420727851878

The article was published by ACG Publications
http://www.acgpubs.org/journal/journal-of-chemical-metrology July-December 2025 EISSN:1307-6183
DOI:http://doi.org/10.25135/jcm.121.2507.3596
Available online: October 27, 2025

vaporize into the air under normal atmospheric conditions of temperature and pressure (i.e., 25 °C, 1 atm) [3]. The concentration of ethanol can decrease by about 2 % at a concentration level of 1 μmol/mol. For ethanol in AL-Acu-IV cylinders, the usual immediate loss was then followed by stability. A different situation was for methanol when the changes in concentration continued [4].

The effect of adsorption could also occur during the analysis of prepared mixtures due to interaction with the internal surface of pipelines. Adsorption of gases is not limited to VOCs. This phenomenon can theoretically occur for all gages. Technically there are two main mechanisms for adsorption. First is based on physisorption and the second is due to chemisorption [5]. The fact that there is a possibility of adsorption of gases on the internal surface of the cylinder is apparent, but how much effort is required to remove adsorbed ethanol is not so clear.

3. Present Study

Preparation of Gas Mixtures: The first step of preparation is the calculation of the future mixture. Calculations are performed according to ISO 6142-1 [6], which explains all formulas necessary for preparation mixtures with various compositions (See Figure S1 in supporting information). The first step is the calculation of the maximum filling pressure, which is important to avoid the condensation of the mixture. The formula for calculating filling pressure is taken from the ISO mentioned above.

$$p_F \leq \frac{1}{\sum_{i=1}^{q}\left[\frac{x_i}{p_i(T_L)}\right]} \tag{1}$$

Where: p_F is filling pressure; x_i is the mole fraction of the component i in the mixture, $i = 1,\ldots,q$; q is the number of components; $p_i(T_L)$ is saturated vapour pressure of component i at temperature T_L.
Filling pressure can be calculated by different approaches. One possible viable way is Antoines equations.

$$lnp_i^0 = A - \frac{B}{(T+C)} \tag{2}$$

Where: p_i^0 is saturated vapour pressure of component I in kPa; A, B and C are empirical constants; T is temperature in kelvins.

Preparation itself is held on differential balances, which allows us to avoid the influence of ambient conditions. Weighting is applied after the addition of every component.

The final composition of the prepared reference materials is calculated according to the formula given in ISO 6142-1.

$$y_k = \frac{\sum_{j=1}^{r}\left(\frac{x_{k,j}\cdot m_j}{\sum_{i=1}^{q} x_{i,j}\cdot M_i}\right)}{\sum_{j=1}^{r}\left(\frac{m_j}{\sum_{i=1}^{q} x_{i,j}\cdot M_i}\right)} \tag{3}$$

Where: y_k is amount of substance fraction of component k in the prepared mixture; $x_{k,j}$ is amount of substance fraction of component k in parent gas; m_j is mass added of parent gas j; $x_{i,j}$ is amount of substance fraction of component i in parent gas j; M_i is the molar mass of the component I individual gas is added to the mixture under continuous weighting. After that the accurate amount is determined on differential balances. The last step of preparation for each mixture involves homogenization to ensure a similar composition of gases in the whole volume of the cylinder. To maintain the stability and homogeneity, it is crucial to follow the storage conditions, mainly the minimum storage temperature.

Differential Scaling: The indisputable and biggest advantage of this approach to weighting of parental gases and liquids is the elimination of influences of ambient conditions, such as temperature, pressure, and humidity. The influence of these quantities is unimportant for weighting for common purposes. In case where high-precision results are required, it is necessary to consider the influence of these quantities. Otherwise, calculations are getting more complicated. For example, the influence of temperature could be calculated according to formula 4.

Desorption of ethanol from the cylinders

$$m = \frac{1-\frac{\rho_a}{\rho_C}}{1-\frac{\rho_a}{\rho}} W \quad (4)$$

Where: m is weight, ρ is density of weighted sample, ρ_a is density of air, ρ_c is density of reference body, W is value of weight (display of scale)

But the density of air must be calculated, formula 5 can be used [7].

$$\rho_a = \frac{0.348444p - h(0.020582)}{273.15+t} \quad (5)$$

Where: ρ_a is the density of air, p is pressure, h is relative humidity, t is temperature
The scaling system in CMI offers not only the elimination of ambient conditions influences. Construction of these scales, which are based on the comparator Mettler-Toledo XP26003L for 5 l and 10 l cylinders. For 40 l cylinders, there is a scale based on the comparator XP64003L. Both scales are equipped with a system for centring the cylinder before weighting. Thus, weighting is not influenced by a different position of the cylinder on the scale. The position is always adjusted by a weighting system.

This approach leads to decreasing the uncertainty of the prepared mixture. An unpleasant disadvantage of this procedure is the necessity to fill gas or liquid into the cylinder before scaling of the scaling system. A pre-weighing balance is used for this purpose. The resolution of this pre-weighing balance is 0.1 g, while the comparator used in the weighting system has a resolution of 0.001 g. Thanks to this, filling itself is realized with lower precision. Until the final quantity of the component is weighed with the highest possible accuracy.

After filling the first component, the amount of the matrix, or the next component, could be recalculated based on the precise quantity of the first added substance. But in the case of all the following substance, this step is not possible. Weighing during filling the cylinder is the most critical part of preparation. The final mass of every added component, m_c, is calculated as follows.

$$m_{cn} = \Delta m_1 - \Delta m_2$$
$$\Delta m_1 = m_{EC} - m_r$$
$$\Delta m_2 = m_{FC} - m_r$$

Where: m_{cn} is the weight of the added component, Δm_1 is the mass difference between the empty cylinder and reference cylinder, Δm_2 is the mass difference between the cylinder filled with component n and the reference cylinder, m_{EC} is the mass of the empty cylinder, m_r is the mass of the reference cylinder, m_{FC} is the mass of the filled cylinder

Evaluation of Mixtures: Evaluation of every prepared mixture is performed on suitable analytical instrumentation based on the character of components in the mixture. The analysis procedure follows the requirements of ISO 6142-1. The determination of the concentration of each component was based on comparison with house standards [8]. During the measurement, analytical instruments offer a response that represents a specific amount of a component in the mixture. This response is compared with the response from analysing house standards.

One of the most important steps in analysis is to choose a proper analytical technique. For VOCs in gaseous mixtures, it is possible to use gas chromatography with flame-ionization detectors. This detector cannot detect nitrogen and other permanent gases. So, it is not necessary to deal with the separation of components on the column.

Determination of Desorption: For the experiment, cylinders were used for the preparation of the ethanol in nitrogen for four years with a concentration of 265 μmol/mol. The cylinders were filled only with ethanol in nitrogen during this period. Subsequently, one cylinder was prepared for filling by normal procedure. The bottle was evacuated for 12 hours to a final pressure less than $1x10^{-2}$ Pa. Then the cylinder

was filled with the 300 grams of nitrogen and kept for the next 12 hours. After that, the cylinder was measured using the standard analytical method generally used for the evaluation of prepared mixtures. Although, the bottle should be without any content of ethanol, ethanol was identified in the analyte Figure 1 chromatogram no. 2. In all chromatographs, there is an artefact represented by the firs peak at time 0.913 min. Results from the analysis were compared to the standard reference materials. But the lowest concentration of those materials is 76 µmol/mol. This concentration was too high for precise evaluation of the concentration of the experimental mixture. Based on the results, it was possible to determine the concentration for the preparation of a new reference mixture.

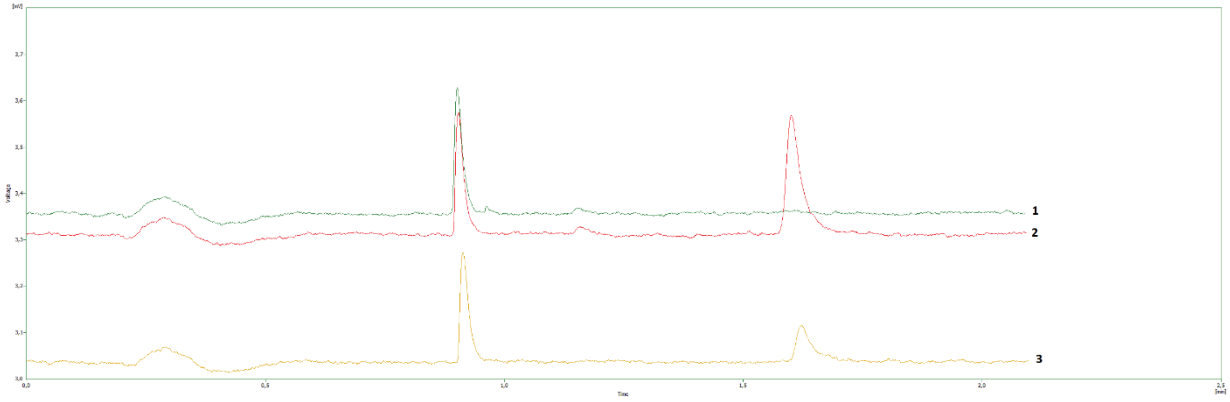

Figure 1. Comparison of chromatograms from analysis experimental mixtures and cylinder after pressure test

Considering this available information, the reference material with concentration 0.1 µmol/mol was prepared as a reference to estimate the real concentration of the mixture, which was created by filling the "clear" cylinder with nitrogen. This reference material was prepared for the cylinder with internal treatment Aculife IV. The concentration of the experimental mixture was determined to be 0.27 µmol/mol.

After finishing the analysis, the bottle with the experimental mixture were emptied and evacuated. Into this cylinder were filled the next 300 grams of nitrogen and kept aside for 12 hours. The new experimental mixture was then analyzed and compared to the reference mixture. Final ethanol concentration of the lates experimental mixture was determined as 0.09 µmol/mol. Figure 1 chromatograph no. 3. Third round of filling and analyzing wasn't performed because of two reasons. First, regarding the achieved results, the final concentration after the third filling would be under the determination limits of analytical instrumentation. Second, the fact that ethanol was adsorbed on the internal surface of the aluminium cylinder without any treatment is indisputable.

Simultaneously with the experimental mixtures, the cylinder was analysed after the pressure test. This cylinder was also used for ethanol in a nitrogen mixture. However, this cylinder was washed with water during the pressure testing and then evacuated. In the case of this cylinder no ethanol was found Figure 1 chromatograph no. 1.

In conclusion, all mixtures involved in this study were prepared in the cylinders with a volume of 40 L, which are commonly used for preparation of reference materials for the verification of alcohol breath analysers. If the ethanol in nitrogen is filled into the aluminium cylinders, there is a risk of adsorption on the internal surface, which can slightly influence the final mixture. After repeated filling, the internal surface of the cylinder is saturated with ethanol. It is not easy to completely remove the adsorbed ethanol from the internal surface just by evacuation the cylinder. For complete removal, it is necessary to wash out the cylinder repeatedly with the matrix. Depending on the prepared concentration, the adsorption should be taken into account. Especially for extremely lower for the calculation of the final concentration, and in all cases, it should be taken into consideration during the calculation of the uncertainty of the prepared mixture. For concentrations in hundreds µmol/mol level prepared into the same cylinders the effect of potential desorption is not necessarily significant.

Acknowledgements

This article is related to my PhD studies at the Slovak University of Technology in Bratislava, Faculty of Mechanical Engineering, focusing on the topic of metrological assurance of addictive substances detection.

Supporting Information

Supporting information accompanies this paper on http://www.acgpubs.org/journal/ journal-of-chemical-metrology

ORCID

Luděk Král: 0009-0006-4040-7309
Jiří Tesař: 0000-0002-5691-4050
Miroslav Bárta: 0009-0001-5487-7495

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