

Gravimetric Preparation of Primary Gas Mixtures with Liquid Component in Air Matrix

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Abstract. This contribution is describing the preparation procedure of primary gas mixtures of ethanol in synthetic air at Slovak Institute of Metrology (SMU). This gas mixture is under the development and in case of good values of repeatability, reproducibility, linearity and stability it should be the part of National standard of mole fraction in gaseous phase (NE 023/99) in SMU.

Keywords: Gravimetric Preparation of Gas Mixtures, Liquid Ethanol, Air Matrix, ND-IR Analyser

1. Introduction

Primary standard gas mixtures (PSMs) are the basis for the disseminating traceability for the analysis of gases. They are prepared by gravimetric method using the weighing of stable gases and volatile liquids into cylinders. Binary gas mixtures prepared at Slovak Institute of Metrology (SMU) are validated on non-dispersive infrared analyser (ND-IR). Determination of the certified values is given by the comparison of measured values with the values of PSMs, which are the part of National Standard. The National standard of mole fraction in gaseous phase has 6 PSMs of ethanol in synthetic air under development. In case of good values of repeatability, reproducibility, linearity and stability it should be the part of National Standard. This contribution is describing the preparation procedure of primary gas mixtures of ethanol in synthetic air at SMU. [1]

2. Subject and Methods

Gravimetric preparation of gas mixtures

The primary gas mixtures are prepared by gravimetric method according to methods that have been widely agreed upon [2].

The gravimetric preparation consists of:

- a) **pre-treatment** (calculations, preparation of suitable cylinder),
- b) **filling of parent gases and liquids into the cylinder,**
- c) **weighing of separate components**

Before starting these circumstances should be taken into account:

- the pressure of parent gases in the cylinders and the pressure of their condensation
- maximum of the filling pressure
- concentration of the parent gases
- methods of filling (directly or by sequential diluting)
- parameters of weighing (uncertainties).

The possibility of the preparation of gas mixture depends on the following conditions: condensation of the components, reaction between the components, interaction between the gases and the inner surface of the cylinder and the parameters of the balances.

The condensation of components can be prevented by lower pressure of filling than is the critical pressure of liquefaction of any from the component at the filling temperature. It is also needed to ensure the suitable temperature during the manipulation and storage of filled cylinders. Before the preparation of gas mixtures it is necessary to investigate, if the components react with each other to prevent possible explosion. The inner surface of the cylinders, valves and pipes should have suitable parameters to prevent the interaction with used gases. [3]

a) Pre-treatment

To obtain as complete composition of the parent gases (purity tables) we measure the purity of the parent gases in our laboratories. Before the starting of the gas mixture preparation it is needed to analyse the pure gases, e.g. the components that will be use in prepared mixture. Amount fraction of the pure gas is calculated according Eq. 1:

$$x_{pure} = 1 - \sum_{i=1}^n x_i \quad (1)$$

where

x_{pure} amount fraction of the pure gas

x_i amount fraction of impurities.

Description of the state of a homogeneous gas mixture and its composition are disclosed in ISO 14912 „Gas analysis – Conversion of gas mixture composition data“. [4] Pre-treatment of the cylinder involves removing the previous gas mixture and then vacuum during 22 hours.

b) Filling of parent gases and liquids into the cylinder

Filling of cylinders by gases is carried out by filling station. Filling can be done on the basis of a different pressure of parent gases, so that the parent gases must have a higher pressure than the gas mixture filled in a cylinder. Generally is preferred order of addition of the component from lowest to highest. The ambient conditions are limited by demands of used devices as turbo molecular pump, diaphragm pump, pressure sensors and vacuum sensors.

Before every filling it is needed to check the filling station, e.g. for leaks on the pipes and the whole way of filling. In case of no leak the vacuum reaches 9×10^{-5} mbar.

c) Weighing of separate components

Relative uncertainties of certified values of amount fractions are on level of 0.1 % , that is why relative uncertainties of the parent gas mass should be under 0.03 %. As the standard uncertainty from weighing is 6 mg, the weighed mass should be 20 g and more.

For weighing separate components we use comparator balances. It should be turn on 4 hours before weighing. We use reference cylinder with approximately same mass as the weighed cylinder. If the difference is smaller than 50 g, we can add to the weighed cylinder maximum 850 g of gas. In case of liquid component we use a syringe for filling it. The mass of the liquid is determined by weighing the full and then the empty syringe on analytical balances. The mass of the added component is calculated from the difference of cylinder masses before and after filling.

After adding of all components we calculate the amount fraction of the component in gas mixture using Eq. 2 shown below and published values of mol masses [5]:

$$x_i = \frac{\sum_{A=1}^p \left(\frac{x_{i,A} \cdot m_A}{\sum_{i=1}^n x_{i,A} \cdot M_i} \right)}{\sum_{A=1}^p \left(\frac{m_A}{\sum_{i=1}^n x_{i,A} \cdot M_i} \right)} \quad (2)$$

where

- x_i amount fraction of the component
 $x_{i,A}$ amount fraction of the component in parent gas
 m_A mass of the added component
 M_i mol mass of the added component

The standard uncertainty of amount fraction is given by:

$$u(x_k) = \sqrt{u_1^2(x_k) + u_{ver}^2(x_k)} \quad (3)$$

where

- $u(x_k)$ standard uncertainty of amount fraction
 $u_1(x_k)$ standard uncertainty from gravimetric preparation
 $u_{ver}(x_k)$ standard uncertainty from verification

The expanded uncertainty of certified value of amount fraction for component k for 2 years is:

$$U(x_k) = 2 u(x_k) \quad (4)$$

Preparation of primary gas mixture of ethanol in synthetic air

Preparation of primary gas mixture of ethanol in synthetic air is carried out by gravimetric method as it is described above. In case of ethanol should be considered its concentration of explosiveness which is 3.3 % - 19.0 % in atmospheric pressure and also the temperature of filling 70 °C. Taking into account all of the above limitations, we have developed preparation scheme showed at Tab.1.

Tab. 1. *Preparation scheme of ethanol in synthetic air*

Preparation scheme of ethanol in air						
x ; mol/mol	0.0008	0.00065	0.00049	0.00026	0.00015	0.00007
P ; bar	35	45	55	80	80	80
$m_{Et,add}$; g	0.26	0.28	0.25	0.07	0.11	0.05
$V_{Et,add}$ 22°C; μ L	330.1	355.4	317.4	253.9	139.6	63.5
$m(N_2)$, g	157.4852	202.5115	247.554	360.162	360.2018	360.2308
$m(O_2)$,g	48.24447	62.03791	75.83626	110.33	110.3448	110.3536
concentration of explosion	0.000943	0.000733	0.0006	0.000413	0.000413	0.000413

We have prepared primary gas mixtures in accordance with this scheme. In this procedure we used both methods of filling – direct method and sequential diluting of the concentrated mixture. At first step we have prepared 3 mixtures for testing the preparation method, the detection limit of the measuring device and for checking the linearity of the calibration curve.

Tab. 2. Primary gas mixtures for testing

No. of cylinder	Cert. compon.	Matrix	xcert. mol/mol	$u(xcert)$. k=1
0078F_3	ethanol	air	0.0000707	0.0000003
9383E_5	ethanol	air	0.00026406	0.00000099
9334E_6	ethanol	air	0.0009643	0.0000025

3. Results

As the results of tested criteria were satisfactory, in the next step we have prepared 6 primary gas mixtures in whole concentration range. These 6 PSMs were checked for its linearity, repeatability, short time stability and reproducibility. Validation of the certified values was carried out on non-dispersive infrared analyser and the difference between the measured value and the value from gravimetric preparation was under 1%.

Tab. 3. Primary gas mixtures of ethanol in air

No. of cylinder	Cert. compon.	Matrix	xcert. mol/mol	$u(xcert)$. k=1
0078F_4	ethanol	air	0.00007191	0.00000059
0695E_11	ethanol	air	0.00015121	0.00000057
9383E_6	ethanol	air	0.0002669	0.000002
0007F_13	ethanol	air	0.0004739	0.0000013
0072F_6	ethanol	air	0.0006684	0.0000017
9334E_7	ethanol	air	0.0008024	0.0000047

It is needed to carry out the long time stability testing of these primary gas mixtures during 2 years and in case of good values of repeatability, reproducibility, linearity and stability it should be the part of National standard of mole fraction in gaseous phase (NE 023/99) in SMU.

4. Conclusions

In this contribution we report the methods and results of gravimetric preparation of binary gas mixtures of ethanol in synthetic air. The results show that the used method of preparation was suitable for this type of gas mixtures.

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