Overview of steps checking traceability of measurement during the process of breath analysers verification using certified reference material.

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Abstract. Breath analysers are measuring devices that in Slovakia must be verified. The verification is done by using certified reference materials of ethanol in nitrogen in 4 concentration levels of ethanol. Here we offer an overview of steps, which are checking the traceability of measurement from the process of verification up to traceability of used reference material to SI unit of mass kg. Each single step is described and has its uncertainty budget.

1. Introduction

The verification of breath analysers is done using certified reference material (CRM) of ethanol in nitrogen in 4 concentrations to cover the full measurement range of the analyser. These CRMs are: 0,00008 mol/mol, 0,00026 mol/mol, 0,0005 mol/mol and 0,0007 mol/mol of ethanol. These CRMs are one after another applied to breath analyser, each 6 times (10 times in case of initial verification) and the measured values are collected for evaluation of maximum permissible errors criteria. The evaluation of these criteria is done using the average value and its uncertainty. That is why we should check the traceability of measurement. Because the fulfil of maximum permissible errors criteria and consequently the authorization to use the breath analyser strongly depends on the uncertainty of measurement, it should be determined by correct way. One of the components of measurement uncertainty determined by method B is the uncertainty of secondary CRM used for verification of breath analyser. The uncertainty of secondary CRM is determined by comparison with primary CRM of ethanol in nitrogen.

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### 2. Single steps of checking traceability

#### 2.1 Verification of breath analysers

For verification of breath analysers we use CRMs of ethanol in nitrogen in 4 concentrations: 0.00008 mol/mol, 0.00026 mol/mol, 0.0005 mol/mol and 0.0007 mol/mol of ethanol in nitrogen. Here is given an example of measurement with the first concentration – 0.00008 mol/mol of ethanol in nitrogen.

Values and their uncertainties measured during the verification of breath analyser:

| Concentration of CRM (mol/mol) | 0.00007868 |
|--------------------------------|------------|
| \( U_{CRM} \) (mol/mol) k=2   | 0.0000007  |
| \( u_{CRM} \) (mol/mol)       | 0.00126    |
| \( u_{CRM} \) (mg/L)          | 0.00000035 |
| \( u_{CRM} \) (mg/L)          | 0.00063    |
| \( u_{CRM} \) (mg/L)          | 0.00029    |
| \( u_{CRM} \) (mg/L)          | 0.00389    |
| \( u_{CRM} \) (mg/L)          | 0.00505    |
| \( u_{CRM} \) (mg/L)          | 0.00029    |
| \( u_{CRM} \) (mg/L)          | 0.0051     |
| \( U_{k=2} \) (mg/L)          | 0.0101     |
| Concentration of CRM (X) (mg/L)| 0.142      |
| Measured values               |            |
| 1                              | 0.131      |
| 2                              | 0.156      |
| 3                              | 0.143      |
| 4                              | 0.147      |
| 5                              | 0.147      |
| 6                              | 0.157      |
| average \( \bar{x}_{aver} \) mg/L | 0.147     |
| difference \( x_{aver} - x_{CRM} \) mg/L | 0.005     |
| abs(difference) + \( u \) (mg/L) | 0.0150    |
| Maximum permissible error mg/L  | 0.020      |

where
- \( u_A \) is the uncertainty determined by method A - standard deviation of 6 measurement,
- \( u_B \) is the uncertainty determined by method B - \( u_{CRM} + u_{ind} \),
- \( u_{CRM} \) is the uncertainty from the CRM used for verification of breath analyser,
- \( u_{ind} \) is the uncertainty from the number of decimal digits, appearing on the breath analyser during the verification,
- \( u_C \) is combined uncertainty.
The result of verification is, that this device fulfil the requirements of maximum permissible error, because the difference between the result of measurement and the reference value is 0,0150 mg/L and the maximum permissible error is 0,020 mg/L.

2.2 Determination of certified value of secondary certified reference material

For verification of breath analysers we use secondary CRMs, with certified values of concentration and their uncertainties. Here are the details of secondary CRM used for verification of breath analysers.

| No. of the CRM certificate | S139/09 |
|----------------------------|---------|
| No. of the CRM cylinder     | 750060  |
| Concentration of CRM (mol/mol) | 0,00007868 |
| $U_{CRM}$ (mol/mol) $k=2$  | 0,0000007 |

Secondary CRMs are prepared by manufacturer and certified values of secondary CRMs are determinate by comparison with primary CRMs of similar concentration.[1] Detailed procedure of certified value determination is given in: Žuriš S, Žurišová Z, Dovica M, Wimmer G: EIV calibration of gas mixture of ethanol in nitrogen. Advanced Mathematical and Computational Tools in Metrology and Testing XI, International Conference, pp.5-6 [2]

For certified value and its uncertainty determination of mixture mentioned above we used primary CRM prepared at our institute.
Secondary CRM: 0,00007868 mol/mol, $U = 0,0000007$ mol/mol
Primary CRM: 0,00008127 mol/mol, $U = 0,00000026$ mol/mol

After the comparison measurement of secondary CRM is calculated the certified value (molar fraction) of secondary CRM $x_C$ and its uncertainty $u(x_C)$ from the response – signal of the measurement system (multimeter connected to nondispersive infrared spectrometer) $y_C$ and its uncertainty $u(y_C)$:

$$y_C = \text{average value from } (y_{C1}, y_{C2}, ...., y_{C10})$$
$$u(y_C) = \left(\frac{1}{\sqrt{10}}\right) \text{ standard deviation from } (y_{C1}, y_{C2}, ...., y_{C10})$$

Molar fractions of component in final mixture $x_C$ are determined from the analytical function $G(y)$.

$$x_C = G(y_C)$$

Parameters of analytic function $G$ are determined by Deming least squares method, where $G$ is suitable function (linear, quadratic, cubic, etc.) characterizing the measured calibration points.

The standard uncertainty is calculated according to law of propagation of uncertainty as [3]

$$u^2(x_C) = \left(\frac{\partial G}{\partial y_C}\right)^2 u^2(y_C) + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial b_i}\right)^2 u^2(b_i) + 2 \sum_{i=1}^{k} \sum_{j=i+1}^{k} \left(\frac{\partial G}{\partial b_i}\frac{\partial G}{\partial b_j}\right) \text{cov}(b_i, b_j)$$

where
- $u(x_C)$ - standard uncertainty of certified value $x_C$ - normal distribution,
- $u(y_C)$ - standard uncertainty of the response - normal distribution,
- $u(b_i)$ - standard uncertainty of the analytical function parameter $b_i$. 

3
cov(b_k, b_1) - covariance between parameters b_k and b_1 evaluated by regression analysis.

The expanded uncertainty $U(x_i)$ is:

$$U(x_i) = k \cdot u(x_i)$$

$k = 2$

2.3 Determination of certified value of primary certified reference material

For certified value and its uncertainty determination of secondary CRM we use primary CRM prepared at our institute.

Primary CRMs prepared at SMU by gravimetric method and the certified values calculated from the weighing of components are validated by analysis of the primary CRMs [4, 5].

By this way our primary CRMs are traceable to unit kg. The purities of parent gases are determined by gas chromatography and they are taken into account during weighing of components.

Here we describe the process of determination of certified value and its uncertainty:

Primary CRM: 0,00008127 mol/mol, $U = 0,00000026$ mol/mol.

Where $U$ is including $u(m)$ standard uncertainty of nitrogen sample weight - normal distribution, $u(M_k)$ standard uncertainty of ethanol sample weight - normal distribution, $u(x_k)$ standard uncertainty of nitrogen impurities - rectangular distribution, validation uncertainty 0,25% - rectangular distribution, mixture stability uncertainty 0,35% - rectangular distribution.

3. Conclusion

In this paper we show a way to check the continuous chain of traceability steps. We described the process of uncertainty investigation in every single step illustrated on real data from breath analysers verification using certified reference material of ethanol in nitrogen. As fulfill of maximum permissible errors criteria strongly depends on the uncertainty of measurement, it should be determined by correct way. Only those breath analysers, that meet the requirements of maximum permissible errors criteria, can get authorization for use as the evidence measurement device.

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