Features of Measurement Method Validation of harmful Substances Concentration in the Air of the working Area

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INTRODUCTION

Today in the Republic of Belarus, there is an acute problem of measurement methods validation of harmful substances concentration in the air of the working area in order to assessment of workplaces on industrial enterprises. Enterprises face the following issues:

-availability of only irrelevant (long developed) measurement procedures;

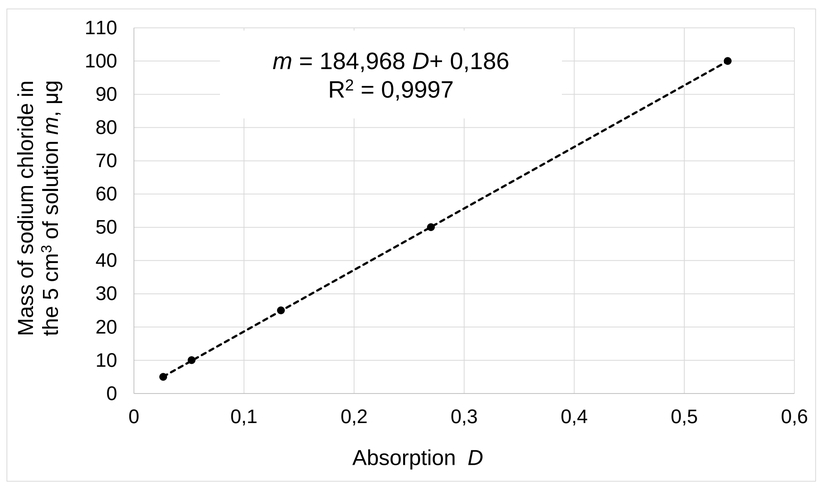
- lack information about performance characteristics of these measurement procedures;

-measurement procedures contain outdated measurement equipment.

We suggest a unified approach to the organization and implementation of validation of such measurement procedures within one laboratory, followed by application of the obtained data for quality control and measurement uncertainty evaluation.

MEASUREMENT METHOD

The most of applied measurements methods are spectrophotometric. Samples were taken through an gas sampler to the filter or into the absorption solution. The substance concentration was determined by the calibration curve with recalculation to the air sample volume that has been taken and reduced to a temperature of 20 ºC and an atmospheric pressure of 101.3 kPa.



Gas sampler ПУ-4Э

Gas sampler ОП-442ТЦ

Concentration of substance

Mass of substance in

$$C = \frac{m \cdot V_1}{V \cdot V_0}$$

Volume of aliquot

Overall volume of solution

Volume of air sample

Atmosphere pressure

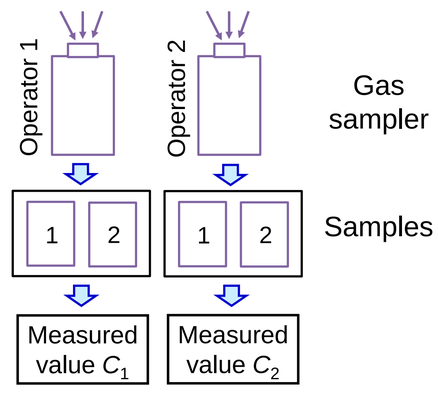
$$V_0 = \frac{293 \cdot V_t \cdot P}{101{,}3 \cdot (273 + t)}$$

Temperature at the sampling point

VALIDATION DESIGN

Key issue is a test sample - AIR. Such matrix is not possible to model. It is hard to achieve acceptable samples homogeneity. Therefore we use:

- real air samples with different substance concentrations in interest to establish detection limits and precisions;
- model samples with a known substance concentration were prepared by spiked pure substance to a clean filter or absorption solution in order to study the laboratory bias of the analytical stage of the measurement procedure.



$$s_I = \sqrt{\frac{\sum_{k=1}^{p} s_k^2}{p}} \qquad s_k = \frac{|C_{1k} - C_{2k}|}{\sqrt{2}}$$

Figure 1 – The scheme of sampling

The real air samples was carried out in one place by two operators simultaneously under the same sampling conditions (Fig. 1). Each operator used his own gas sampler. This scheme was implemented at least 10 times on each concentration level in interest ($p \geq 10$ measurement series were obtained). We think that samples taken simultaneously are homogeneity enough. Standard deviations of repeatability and precision in intermediate conditions were calculated based on difference of measured values obtained on samples from one series in accordance to EURACHEM Guide[1] and ISO 5725[2].

We can examine only the laboratory bias of the analytical stage of the measurement procedure within intralaboratory validation. The number of prepared model samples was not less than 10 for each concentration level in interest. The model samples from one concentration level were measured in the repeatability condition. Student’s *t*-test was used to determine if the bias of measurement method are significantly different from zero.

Bias

$$t = \frac{|\Delta_{bias}|}{\sqrt{\frac{s^2}{p} + u^2(C_{ref})}}$$

Standard deviation of results, obtained to calculate bias

Number of results

Standard uncertainty of reference value

Samples were taken or prepared at least on three concentration levels from the measurement range of the procedure including the value of the maximum permissible concentration to establish the dependence of accuracy parameters on the measured value level.

RESULTS AND DISCUSSION

The results of determination of accuracy parameters on the example of measurement procedure of sodium chloride concentration in air are presented in the tables 1 and 2.

Table 1 – Determination of precision of measurement procedure of sodium chloride concentration in air

Level of sodium chloride concentration, mg/m³	Repeatability standard deviation		Intermediate precision standard deviation	
	s_r, mg/m³	s_{ro}, %	s_I, mg/m³	s_{Io}, %
0,8743	0,0789	9,0	0,0496	5,7
1,8891	0,0798	4,2	0,0891	4,7
4,5549	0,1670	3,7	0,1881	4,1

Table 2 – Determination of bias of measurement procedure of sodium chloride concentration in air and results of Student’s t-test application

Reference value, mg/m³	Standard uncertainty of reference value, mg/m³	Level of sodium chloride concentration, mg/m³	Standard deviation of results, mg/m³	Bias, mg/m³	Student Statistics, t_i
1,000	0,014	0,973	0,0383	–0,0270	1,471
2,500	0,019	2,463	0,0750	0,0370	1,212
5,000	0,069	5,052	0,0925	0,0519	0,691
9,000	0,082	8,947	0,0997	–0,0533	0,607
14,000	0,150	14,081	0,1388	0,0806	0,517

Critical value $t_{0,05;9}$ = 2,262, degrees of freedom is 9, significance level is 5 %

Based on validation data of various measurement methods of harmful substances concentration in the air of the working area, it can be noted:

- the intermediate precision standard deviation (arithmetic means of two parallels measurements, obtained by two operators) in the whole investigated range of measurement procedures is numerically comparable with the repeatability standard deviation (results obtained on two parallels by one operator);
- analytical laboratory bias for the whole range of concentrations of measurement procedures is insignificant relative to the precision;
- sampling, calibration, and precision are the main sources of uncertainty.

CONCLUSION

The proposed validation design has applied on the enterprises of the Republic of Belarus and, in the opinion of the authors, it is optimal for the purposes of intralaboratory validation of measurement methods of harmful substances concentration in the air of the working area.

REFERENCES

1. EURACHEM Guide “*The Fitness for Purpose of Analytical Methods. A Laboratory Guide to Method Validation and Related Topics*”, Second edition, 2014
2. ISO 5725:1994 *Accuracy (trueness and precision) of measurement methods and results* (Parts 1-3)