International Key Comparison

COOMET.QM-S3.2015 (COOMET project № 664/RU/14)
Supplementary comparison of standard gas mixtures “Atmospheric air pollutants: CO in Nitrogen, 5 μmol/mol”

Saint-Petersburg
2016
Supplementary comparison COOMET. QM-S3.2015 (COOMET 664/RU/14)

Final report
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Field
Amount of substance: gas analysis

Subject
Supplementary comparison of standard gas mixtures “Atmospheric air pollutants: CO in Nitrogen, 5 µmol/mol”

Participants:

<table>
<thead>
<tr>
<th>Institute</th>
<th>City</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>VNIIM</td>
<td>St. Petersburg</td>
<td>Russia</td>
</tr>
<tr>
<td>BelGIM</td>
<td>Minsk</td>
<td>Belarus</td>
</tr>
<tr>
<td>KazInMetr</td>
<td>Karaganda</td>
<td>Kazakhstan</td>
</tr>
</tbody>
</table>

Organising body
TC 1.8 «Physical Chemistry» COOMET

Background

Carbon monoxide (CO) is present in atmosphere due to different natural and anthropogenic sources. Ambient CO ranges from 50 nmol/mol to 300 nmol/mol at marine boundary and from 100 nmol/mol to 500 nmol/mol at city area. Carbon monoxide is a toxic gas and in concentrations higher than (3-5) µmol/mol it is hazardous to human health.

The first key comparison on carbon monoxide in nitrogen dates back to 1992 (CCQM-K1a). Gas mixtures of CO in nitrogen belong to one of the first type of gas mixtures that were used in international key comparisons. Since then, numerous national metrology institutes (NMIs) have been setting up facilities for gas analysis, and have developed claims for their calibration and measurement capabilities (CMCs) for these mixtures.

During past years there were carried out few comparisons on this topic: EUROMET 900a (2007), CCQM-K51 (2009) and COOMET.QM-S3 (2014).
**Supported claims**

This supplementary comparison aims to support CMC claims for carbon monoxide from $1 \mu\text{mol/mol}$ and higher in a nitrogen matrix. This comparison can also be used to support CMC claims for carbon monoxide in an air matrix with special consideration for cross interference from the high concentration of oxygen on the CO concentrations especially with measurement techniques, such as NDIR.

**Measurement standards**

The nominal amount of substance fraction of the component in gas mixtures was:

- CO: $5.0 \mu\text{mol/mol}$
- N$_2$: balance.

The total number of gas mixtures that took part in these comparisons was 4. All gas mixtures were prepared during this comparison. Two gas mixtures were sent to participants for the study. Two other gas mixtures were left in VNIIM for stability study.

**Schedule**

The cylinders containing the comparison mixtures were shipped to all the participants in August 2015. The measurement results were submitted by the participants in October–November 2015. All cylinders were returned to the coordinating laboratory in November – December 2015. Reanalysis of gas mixtures in the coordinating laboratory was carried out in January 2016.

**Measurement protocol**

The protocol informed the participants about the ranges of nominal concentration of the component in the gas mixtures. The measurement protocol requested each laboratory to perform at least 3 measurements under repeatability conditions with separate calibration before and/or after each measurement. Reports of the laboratories were to contain information on the methods that were used for analyzing the comparison gas mixtures, calibration methods, methods of preparation of calibration mixtures, and also a detailed uncertainty budget.

**Measurement model**

The measurement model has been taken from the key comparison CCQM-K51 [1]. The gas mixtures for the comparison were prepared gravimetrically in accordance with the requirements of ISO 6142-1:2015 [2] and were studied regarding their composition and stability at the coordinating laboratory (VNIIM) in accordance with requirements of ISO 6143:2011 [3]. The amount–of–substance fractions as obtained from gravimetry and purity analysis of the parent substances were used as reference values.

The combined standard uncertainty of a component reference value $u_{i,\text{ref}}$ (for a mixture $i$) was calculated using the following equation:

$$u_{i,\text{ref}} = \sqrt{u_{i,\text{grav}}^2 + u_{i,\text{ver}}^2 + u_{i,\text{stab}}^2}$$  \hspace{1cm} (1)

where
\( u_{i, \text{grav}} \) – is the standard uncertainty of gravimetric preparation.

The following equation is used to calculate the combined uncertainty of the gravimetric uncertainty:

\[
    u_{i, \text{grav}} = \sqrt{u_{i, \text{weighing}}^2 + u_{i, \text{purity}}^2}
\]

- \( u_{i, \text{weighing}} \) - is the standard uncertainty of weighing process;
- \( u_{i, \text{purity}} \) - is the standard uncertainty due to the purity of the parent gases;
- \( u_{i, \text{ver}} \) - is the standard uncertainty from verification;
- \( u_{i, \text{stab}} \) - is the standard uncertainty due to instability.

Long-term stability measurements did not show any change in the concentration of the target components within the precision of these measurements, so that there was not any corrections due to instability.

The standard uncertainty due to instability was taken as zero: \( u_{i, \text{stab}} = 0 \).

Thus an expression for the combined standard uncertainty of a reference value was calculated as:

\[
    u_{i, \text{ref}} = \sqrt{u_{i, \text{grav}}^2 + u_{i, \text{ver}}^2}
\]

### Measurement methods and calibration procedures

The following methods of measurement and calibration have been employed

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Measurement method</th>
<th>Calibration method</th>
<th>Total number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>VNIIM</td>
<td>CRDS</td>
<td>One point calibration</td>
<td>3 measurements 10 sub-measurements</td>
</tr>
<tr>
<td>BelGIM</td>
<td>NDIR analyzer</td>
<td>Calibration curve with three points</td>
<td>6 measurements with 60 sub-measurements</td>
</tr>
<tr>
<td>KazInMetr</td>
<td>Gas chromatography with flame ionization detector (FID) + methanator</td>
<td>Calibration curve with three points</td>
<td>3 measurements 5 sub-measurements</td>
</tr>
</tbody>
</table>

### Degrees of equivalence

The degree of equivalence \((D_i)\) for each participating laboratory is defined in accordance with the equation:

\[
    D_i = x_{i, \text{lab}} - x_{KCRV}
\]

Since the comparison gas mixtures had slightly different amount fractions and taking into account the fact that the coordinating laboratory prepared the mixtures using the same methods and materials, the individual values based on gravimetry and purity analysis can be adopted as reference values.

Hence the degree of equivalence can be expressed as:
\[ D_i = x_{i,\text{lab}} - x_{i,\text{ref}} \]  \hspace{1cm} (5)

The combined standard uncertainty of the degree of equivalence can be expressed as

\[ u(D_i) = \sqrt{u_{\text{lab}}^2 + u_{\text{grav}}^2 + u_{\text{ver}}^2} \]  \hspace{1cm} (6)

The expanded uncertainty \( U(D_i) \) at a 95 % confidence level is calculated using the following equation:

\[ U(D_i) = k \sqrt{u_{\text{lab}}^2 + u_{\text{grav}}^2 + u_{\text{ver}}^2} \]  \hspace{1cm} (7)

where \( k \) is the coverage factor (\( k=2 \)).

The degrees of equivalence for the participating laboratories are shown relative to the gravimetric values in the figure 1. For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been assumed. For obtaining the standard uncertainty of the laboratory results, the expanded uncertainty (stated at a confidence level of 95 %) from the laboratory was divided by the reported coverage factor.

**Results**

In this section the results of the comparison are summarized. In the Table 2 the following data is presented:

- \( x_{i,\text{ref}} \): reference value (amount of substance fraction from gravimetric preparation), \( \mu\text{mol/mol} \);
- \( u_{i,\text{ref}} \): uncertainty of the reference value, \( \mu\text{mol/mol} \);
- \( x_{i,\text{lab}} \): result of laboratory, \( \mu\text{mol/mol} \);
- \( u_{i,\text{lab}} \): stated standard uncertainty of laboratory, \( \mu\text{mol/mol} \);
- \( D_i \): degree of equivalence (difference between laboratory result and reference value), \( \mu\text{mol/mol} \);
- \( U(D_i) \): expanded uncertainty of \( D_i \), at 95 % level of confidence, \( \mu\text{mol/mol} \);
- \( k \): assigned coverage factor for degree of equivalence;
- \( D_{i,\text{rel}} \): relative form for degree of equivalence (\( D_{i,\text{rel}} = D_i \cdot 100/ x_{i,\text{ref}} \), %);
- \( U(D_i)_{\text{rel}} \): relative form for expanded uncertainty of degree of equivalence (\( U(D_i)_{\text{rel}} = U(D_i) \cdot 100/ x_{i,\text{ref}} \), %).
<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Cylinder</th>
<th>$x_{i,grav}$ (µmol/mol)</th>
<th>$u_{i,ref}$ (µmol/mol)</th>
<th>$x_{i,lab}$ (µmol/mol)</th>
<th>$u_{i,lab}$ (µmol/mol)</th>
<th>$D_i$ (µmol/mol)</th>
<th>$D_i / x_{i,grav}$ %</th>
<th>k</th>
<th>$U(D_i)$ (µmol/mol)</th>
<th>$U(D_i) / x_{i,grav}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>VNIIM</td>
<td>D247575</td>
<td>5.0197</td>
<td>0.003</td>
<td>5.0205</td>
<td>0.004</td>
<td>0.0008</td>
<td>0.016</td>
<td>2</td>
<td>0.010</td>
<td>0.199</td>
</tr>
<tr>
<td>BelGIM</td>
<td>D958509</td>
<td>5.0125</td>
<td>0.003</td>
<td>4.93</td>
<td>0.06</td>
<td>-0.082</td>
<td>-1.646</td>
<td>2</td>
<td>0.120</td>
<td>2.394</td>
</tr>
<tr>
<td>KazInMetr</td>
<td>D249246</td>
<td>5.0002</td>
<td>0.003</td>
<td>5.028</td>
<td>0.055</td>
<td>0.028</td>
<td>0.556</td>
<td>2</td>
<td>0.110</td>
<td>2.200</td>
</tr>
</tbody>
</table>
Figure 1. Degrees of equivalence
Discussion and Conclusions

The results are consistent with the reference values. The observed differences between the reference and reported values are within ± 1.7 % relative to the gravimetric values, and do not exceed the appropriate assigned expanded uncertainties.

References

[1] Angelique Botha; Mellisa Janse van Rensburg; James Tshilongo; Nompumelelo Leshabane; Napo Ntsasa; Kenji Kato; Nobuhiro Matsumoto; Volker Stummer; L.A. Konopelko; Y.A. Kustikov; V.V. Pankraov; I.I. Vasserman; C.V. Zavyalov; E.V. Gromova; Ian Uprichard; Gergely Vargha; M. Maruyama; Hans-Joachim Heine; Francisco Rangel Murillo; Victor M. Serrano Caballero; Alejandro Perez Castorena; Tatiana Mace; Franklin Guenther; Walter Miller; Andres Rojo; Teresa Fernandez; Dariusz Cieciora; Valnei S. Cunha; Claudia C. Ribeiro; Cristiane R. Augusto; Han Qiao; Zeui Zhou; Damian Smeulders; Michel Gerboles; Matej Kapus; Rob M Wessel; Florbela Dias; Goncalo Baptista; Prabhat K. Gupta; P Johri; Bunthoorn Laongsri; Ratirat Sinweeruthai; Bernhard Niederhauser; Andreas Ackermann; Marina Froehlich; Andreas Wolf; Jeongsoon Lee; Stanislav Musil; Miroslaiva Valkova; Jari Walden; Sisko Laurila, International Comparison CCQM-K51, Final Report


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Completion Date
January 2016
Annex A

Reports submitted by participating laboratories
BelGIM report

**COOMET No 664/RU/14**

"Atmospheric gases contaminants: CO in nitrogen 5 µmol/mol"

REPORT ON RESULTS OF THE STUDY

I. Results of experimental study

*Laboratory:* Belarus, BelGIM, Section for physicochemical and optical measurements, sector for standards and gas mixtures, 8, Serova st., Minsk.

*Cylinder No:* D958509.

<table>
<thead>
<tr>
<th>Component</th>
<th>Date dd/mm/yy</th>
<th>Result, µmol/mol</th>
<th>Standard deviation, % rel.</th>
<th>No of observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon oxide</td>
<td>02.10.15</td>
<td>4.94</td>
<td>0.06</td>
<td>60</td>
</tr>
<tr>
<td>Carbon oxide</td>
<td>06.10.15</td>
<td>4.99</td>
<td>0.08</td>
<td>60</td>
</tr>
<tr>
<td>Carbon oxide</td>
<td>07.10.15</td>
<td>5.03</td>
<td>0.06</td>
<td>60</td>
</tr>
<tr>
<td>Carbon oxide</td>
<td>09.10.15</td>
<td>4.93</td>
<td>0.09</td>
<td>60</td>
</tr>
<tr>
<td>Carbon oxide</td>
<td>13.10.15</td>
<td>4.93</td>
<td>0.23</td>
<td>60</td>
</tr>
<tr>
<td>Carbon oxide</td>
<td>02.11.15</td>
<td>4.78</td>
<td>0.34</td>
<td>60</td>
</tr>
</tbody>
</table>

**Final results:**

<table>
<thead>
<tr>
<th>Component</th>
<th>Result, µmol/mol</th>
<th>Coverage factor</th>
<th>Expanded uncertainty, µmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon oxide</td>
<td>4.93</td>
<td>2</td>
<td>0.12</td>
</tr>
</tbody>
</table>

II. Description of examinations

**Equipment**

Measurements were carried out using gas analyzer (hereinafter – GA) GIAM-15М, operation principle – infrared optoacoustic.

Delivery and supporting of the sample constant flow rate was carried out using electronic regulator of the mass flow rate (manufacturer - "Eltochpribor", Russia).

Receiving and processing data from gas analyzer was carried out using computer and specialized software (own development).

In order to process measurement results the system of receiving data from gas analyzer GIAM -15M into computer was developed on the basis of 8-channel CP/CAP "ADCS14-8D".
Operation principle is as follows: GIAM-15M provides analogue signal via interface "current loop" 4-20 mA. On the load resistor 510 Ohm voltage is created that is proportional to the gas analyzer measurement results. Voltage is measured on ACP of multichannel block ADCS14-8D and transferred into computer via interface RS232. Data is received by special program GIAM15.exe, that ensures (in addition to data receiving) automatization of calibration, calculation of the results in the units of gas content in mixtures (μmol/mol) and saving of data packages received in the file in .xls format (Excel).

During measurement carrying out the following additional devices and materials were used:
1. Nitrogen, specification "6.0";
2. Two-step pressure regulators with metallic membranes;
3. Two-component gas mixtures prepared and attested by gravimetric method.

Calibration gas mixtures - calibration standarts (hereinafter –CS).
Quantitative compound of CS was determined by gravimetric method according to ISO 6142:2001.
Component content in CS is expressed in mol fractions. Uncertainty of CS compound is expressed as standard uncertainty. Molar masses of the components and their uncertainties are taken from ISO 14912:2003(E).
Data on the source gases purity are taken from supplier specifications and from the results of the analysis according to measurement method for impurity content in pure gases, developed in BelGIM.
In order to prepare mixtures nitrogen (specification "6.0") was used. Final mixtures are obtained by using 3-time dilution: 100 % → 1 % → 200 mol/mol → final mixture.

Gas analyzer calibration and standard reference materials measuring

1. When carrying out GA calibration, CS were used the composition of which was identical to the composition of the sample being analyzed. Each CS component contents with associated standard uncertainties are given in Table 3

<table>
<thead>
<tr>
<th>Cylinder No, date of preparation</th>
<th>CO content, μmol/mol</th>
<th>Standard uncertainty, μmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Н2627, 16.09.2015</td>
<td>4,054</td>
<td>0,011</td>
</tr>
<tr>
<td>Н2613, 17.09.2015</td>
<td>5,072</td>
<td>0,013</td>
</tr>
<tr>
<td>Д2234, 18.09.2015</td>
<td>10,01</td>
<td>0,03</td>
</tr>
</tbody>
</table>

2. Number of sub-measurments. When receiving data, the program plots the signal graphic, which displays drift/drop/rise of the signal. Measurement result is moving average of the last 60 values (the frequency of data reception – 1 sec) in the absence of signal drift.

3. Analytical function (hereinafter - AF) used to determine the content of component in a sample being analyzed is written as follows:

\[ x(y) = b_1 y + b_0 \]  

where: \( x \) – CO content, μmol/mol;
\( y \) - value of the GA response, μmol/mol;
\( b_1 \) - slope coefficient;
\( b_0 \) - intercept coefficient.

4. Upon completion of calibration calculations of analytical function coefficients were made according to ISO 6143:2001, and also uncertainties of values of angular
coefficients and their covariation were calculated using the program recommended in the above-mentioned standard.

**Uncertainty calculation**

Generally, the total standard uncertainty related to results of 4 individual measurements, is evaluated by following formula:

\[ u(x) = \sqrt{u_A^2 + u_B^2} \]

(2)

where \( u_A \) - uncertainty associated with results of individual measurements;

\( u_B \) - uncertainty due to GA calibration and to the uncertainty of CS CO contents.

**A-type uncertainty evaluation**

The A-type uncertainty \( u_A \) of the results of \( n=6 \) measurement series is evaluated by the formula:

\[ u_A = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n(n-1)}}. \]

(3)

<table>
<thead>
<tr>
<th>Component</th>
<th>Meas. 1</th>
<th>Meas. 2</th>
<th>Meas. 3</th>
<th>Meas. 4</th>
<th>Meas. 5</th>
<th>Meas. 6</th>
<th>Mean</th>
<th>( u_A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>4,94</td>
<td>4,99</td>
<td>5,03</td>
<td>4,93</td>
<td>4,93</td>
<td>4,78</td>
<td>4,93</td>
<td>0,04</td>
</tr>
</tbody>
</table>

**B-type uncertainty evaluation**

B-type uncertainty \( u_B \) due to the uncertainty of CS component contents and to the uncertainty of the GA response to those content during its calibration was evaluated on the basis of results of calibration measurements for each measurement series.

Generally, the uncertainty of results of component determination for each series of measurements is evaluated by the following formula

\[ u(x) = \sqrt{(b_1)^2 \cdot u^2(y) + u^2(b_0) + y^2 \cdot u^2(b_1) + 2 \cdot y \cdot u(b_1, b_0)}. \]

(4)

where \( u(y) \) - standard uncertainty of the GA response \( y \); 
\( u(b_1) \) - standard uncertainty of the AF slope coefficient; 
\( u(b_0) \) - standard uncertainty of the AF intercept; 
\( u(b_1, b_0) \) - covariation of the AF arguments \( b_0 \) and \( b_1 \).

Taking \( y(u)=0 \) we obtain the uncertainty associated with the GA calibration.

<table>
<thead>
<tr>
<th>Component</th>
<th>Meas. 1</th>
<th>Meas. 2</th>
<th>Meas. 3</th>
<th>Meas. 4</th>
<th>Meas. 5</th>
<th>Meas. 6</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0,028</td>
<td>0,04</td>
<td>0,03</td>
<td>0,02</td>
<td>0,028</td>
<td>0,022</td>
<td>0,04</td>
</tr>
</tbody>
</table>

**Total standard uncertainty evaluation results.**

<table>
<thead>
<tr>
<th>Component</th>
<th>( x ), ( \mu )mol/mol</th>
<th>( u_A ), ( \mu )mol/mol</th>
<th>( u_B ), ( \mu )mol/mol</th>
<th>( u(x) ), ( \mu )mol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>4,93</td>
<td>0,04</td>
<td>0,04</td>
<td>0,06</td>
</tr>
</tbody>
</table>
**KazInMetr report**

International Key Comparison
COOMET.QM-S3.2015 (COOMET project № 664/RU/14)
Supplementary comparison of standard gas mixtures
“Atmospheric air pollutants: CO in Nitrogen, 5 µmol/mol”

Laboratory: Karaganda branch of RSE "Kazakhstan Institute of Metrology" Republic of Kazakhstan
Cylinder number: D249246

I. Measurement

<table>
<thead>
<tr>
<th>Measurement #1</th>
<th>Date</th>
<th>Result, µmol/mol</th>
<th>Standard deviation (% relative)</th>
<th>Number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>20.09.15</td>
<td>5,025</td>
<td>0,46</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measurement #1</th>
<th>Date</th>
<th>Result, µmol/mol</th>
<th>Standard deviation (% relative)</th>
<th>Number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>20.09.15</td>
<td>5,018</td>
<td>0,60</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measurement #1</th>
<th>Date</th>
<th>Result, µmol/mol</th>
<th>Standard deviation (% relative)</th>
<th>Number of replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>21.09.15</td>
<td>5,041</td>
<td>0,73</td>
<td>5</td>
</tr>
</tbody>
</table>

Result

<table>
<thead>
<tr>
<th>Component</th>
<th>Result, µmol/mol</th>
<th>Coverage factor*)</th>
<th>Expanded Uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>5,028</td>
<td>2</td>
<td>0,110</td>
</tr>
</tbody>
</table>

*) The coverage factor based on 95 % confidence.
II. Measurement Details for COOMET.QM-S3.2015

Instruments

Measurements were carried out using gas chromatograph "Crystal 5000" combined with flame-ionization detector and methanazer for conversion carbon monoxide.

Carrier gas: argon.
Volume size: 1 ml.
Chromatographic column: Carboxen 1000, 3m x 2mm.
Computers and software "Chromatech Analytic” were used to control chromatograph and collect and process chromatographic data.

Calibration standards

1. The calibration gas standards were prepared by gravimetric method multiple dilutions, according to ISO 6142. An electronic mass-comparator (Mettler Toledo model XP10003S, capacity 10.1 kg, readability 1 mg) was used for preparation of all calibration gas standards. Manufacturer, type and metrological characteristics of the equipment used for the preparation of the gravimetric gas mixtures are given in Table 1.

<table>
<thead>
<tr>
<th>Type</th>
<th>Manufacturer</th>
<th>Metrological characteristics</th>
</tr>
</thead>
</table>
| Model XP10003S | «Mettler-Toledo», Swizerland | The maximum limit weighing 10100 g  
Resolution 1 mg  
The standard deviation of 10 mg  
The maximum change in temperature for 1 h. ± 0.5 ° C |
| Gas mixing plant, GSU-3 | OOO «PGS-Servise», Russian Federation | Pressure measuring range:  
from 0.001 to 16.0 MPa  
Residual pressure cylinders before filling 10 Pa.  
Диапазон измерения давления:  
от 0,001 до 16,0 МПа  
Остаточное давление баллонов перед наполнением 10 Па. |

For the production of calibration gas mixtures were used aluminum cylinders with a capacity of 4 dm3 complete with brass diaphragm valve type VBM-1. The internal surface of the cylinders was coated by paraffin grade P2.

2. Analysis of the purity of the clean gases.

Analysis of the purity of the original pure gases was based on information provided by the suppliers of pure gases (passports, certificates), as well as on the results of the measurement of impurities in pure gases using measurement techniques developed and approved by the RSE "KazInMetr".

In cases where the analytical method can not determine the content of the alleged impurities molar fraction of the expected impurity was assumed to be half the detection limit of the analytical method. The content of impurities unmeasured assumes a rectangular probability distribution, whereby the standard uncertainty is calculated as half the detection limit.

Determination of impurities in the starting pure gases (carbon monoxide, nitrogen) used to prepare calibration samples was conducted by gas chromatography using a flame
ionization, thermal chemical and thermal conductivity detector.

The content of impurities in the pure gas used for preparing the calibration gas mixtures shown in Table 2.

Table 2.

The metrological characteristics of pure gases.

<table>
<thead>
<tr>
<th>Clean gas</th>
<th>Component</th>
<th>Content mole fraction, %</th>
<th>The standard uncertainty, mole fraction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>99,588</td>
<td>0,1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N2</td>
<td>99,98</td>
<td>0,01</td>
</tr>
</tbody>
</table>

In measuring the mass of gas filled and comparative cylinder identical volume being weighed according to the scheme and the method of substitution RMMR.

Based on previous studies RMS measurement result is taken to be 30 mg (standard uncertainty evaluated by type A).

3. After making the balloon with the calibration gas mixture was placed in a laboratory, where the at least 72 hours. Before the measurement tanks rolled the calibration gas mixtures for 10 minutes.

**Calibration of instrument**

1. Calibration was performed using GC calibration gas mixtures are identical in composition to sample comparisons. The content of each component and its expanded uncertainty (k = 2) is shown in Table 3.

Table 3 - Calibration gas mixtures

<table>
<thead>
<tr>
<th>Cylinder number, passport number, size, material, date of manufacture</th>
<th>Component</th>
<th>Content, x (µmol/mol)</th>
<th>The standard uncertainty of the calibration samples (rel.), U (x),%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV-146, 09.2015 r. 4dm³</td>
<td>CO</td>
<td>6,147</td>
<td>0,3</td>
</tr>
<tr>
<td></td>
<td>N2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PV-148, 09.2015 r. 4dm³</td>
<td>CO</td>
<td>4,297</td>
<td>0,3</td>
</tr>
<tr>
<td></td>
<td>N2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PV-149, 09.2015 r. 4dm³</td>
<td>CO</td>
<td>5,209</td>
<td>0,3</td>
</tr>
<tr>
<td></td>
<td>N2</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

The total content of components standard uncertainty in calibration gas mixtures are calculated according to the formula:
The standard uncertainty of the molar mass of gases, as well as uncertainty due to air buoyancy, with the pressure and volume of a cylinder is filled not taken into account in connection with a minor contribution.

2. The measurements were carried out under repeatability conditions. Before each measurement was conducted by the chromatograph calibration of 3 models (PV-146, PV-148, PV-149). Each measurement includes 5 observations.

3. Analytical function used to determine the components in the sample is as follows:

$$x(y) = b_1 y + b_0$$

where,

$x$ – measured content, мкмоль/моль;

$y$ – chromatographic response of the analyte;

$b_1$ – coefficient of linear dependence;

$b_0$ – offset coefficient.

**Sample preparation**

The sample with the sample and the calibration sample was stored prior to measurement for 24 hours in the laboratory. The change in temperature in the laboratory at the time of measurement is ± 2 ° C, the change in pressure within ± 0,5 kPa.

**Calculation of measurement uncertainty**

Uncertainty value $u(x)$ was calculated in accordance with ISO 6143 taking into account the uncertainties of the calibration standards and instrument response variability during calibration and measurements under reproducibility conditions:

$$u(x) = \sqrt{u^2(x,x_{cs}) + u^2(x,y)}$$

were

$u(x,x_{cs})$ – the standard uncertainty associated with the amount-of-substance fractions of the calibration standards;

$$u(x,x_{cs}) = \sqrt{\sum_{i=1}^{n} \left( \frac{u(x_{cs_i})}{n} \right)^2}.$$
where
\( u(x_{ci}) \) – uncertainty of the calibration standards;
\( n \) - number of the calibration standards;
\( u(x, y) \) – uncertainty associated with the instrument response,

\[
u(x, y) = \sqrt{\frac{u^2(y) + x^2(u_a) + 2x \cdot \text{cov}(a_0, a_1) + u^2(a_0)}{a_1^2}},
\]

where
\( u(y) \) – uncertainty of instrument response during measurements;
\( a_0, a_1, u(a_0), u(a_1), \text{cov}(a_0, a_1) \) – calibration function parameters obtained from B_Least for linear function.
The calibration function parameters of all measurements are given in Table 7.

### Table 4 - Calibration function parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1(^{\text{st}}) measurement</th>
<th>2(^{\text{nd}}) measurement</th>
<th>3(^{\text{rd}}) measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression coefficient ( a_0 )</td>
<td>-3,546405·100</td>
<td>-2,875126·100</td>
<td>-6,430060·100</td>
</tr>
<tr>
<td>Regression coefficient ( a_1 )</td>
<td>3,666565·101</td>
<td>3,650333·101</td>
<td>3,638941·101</td>
</tr>
<tr>
<td>Regression coefficient uncertainty ( u(a_0) )</td>
<td>3,471791·100</td>
<td>3,444038·100</td>
<td>5,862523·100</td>
</tr>
<tr>
<td>Regression coefficient uncertainty ( u(a_1) )</td>
<td>7,062700·10-1</td>
<td>6,957755·10-1</td>
<td>1,147168·100</td>
</tr>
<tr>
<td>Covariance ( \text{cov}(a_0, a_1) )</td>
<td>-2,428161·100</td>
<td>-2,375225·100</td>
<td>-6,652683·100</td>
</tr>
</tbody>
</table>

### Table 5

#### Uncertainty table

<table>
<thead>
<tr>
<th>Uncertainty source ( X_i )</th>
<th>Estimate ( x_i )</th>
<th>Assumed distribution</th>
<th>Standart uncertainty ( u(x_i) )</th>
<th>Sensitivity coefficient ( c_i )</th>
<th>Contribution to standard uncertainty ( u_f(y) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncertainty associated with the amount of substance fractions of the calibration standards</td>
<td>-</td>
<td>Нормальное</td>
<td>0,01 μmol/mol</td>
<td>1</td>
<td>0,01 μmol/mol</td>
</tr>
<tr>
<td>Uncertainty associated with the instrument response</td>
<td>-</td>
<td>Нормальное</td>
<td>0,054 μmol/mol</td>
<td>1</td>
<td>0,054 μmol/mol</td>
</tr>
</tbody>
</table>

Coverage factor: \( k = 2 \).

Expanded uncertainty: 0,110 μmol/mol.
Supplementary comparison of standard gas mixtures “Atmospheric air pollutants: CO in Nitrogen, 5 µmol/mol”

I. Results of Study

Laboratory: D.I. Mendeleyev Institute for Metrology (VNIIM), Research Department of the State Standards in the Field of Physico-Chemical Measurements

Cylinder number: D247575
Nominal Composition:
- Carbon monoxide: 5 µmol/mol
- Nitrogen: balance

<table>
<thead>
<tr>
<th>Measurement №</th>
<th>Component</th>
<th>Date</th>
<th>Result, (µmol/mol)</th>
<th>Standard deviation, % relative</th>
<th>number of sub measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>№1</td>
<td>Carbon monoxide</td>
<td>08.07.2015</td>
<td>5.0198</td>
<td>0.16</td>
<td>10</td>
</tr>
<tr>
<td>№2</td>
<td>Carbon monoxide</td>
<td>09.07.2015</td>
<td>5.0210</td>
<td>0.18</td>
<td>10</td>
</tr>
<tr>
<td>№3</td>
<td>Carbon monoxide</td>
<td>10.07.2015</td>
<td>5.0209</td>
<td>0.17</td>
<td>10</td>
</tr>
</tbody>
</table>

**Final results:**

<table>
<thead>
<tr>
<th>Component</th>
<th>Result (assigned value), µmol/mol</th>
<th>Coverage factor</th>
<th>Expanded uncertainty (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>5.021</td>
<td>2</td>
<td>0.008</td>
</tr>
</tbody>
</table>
II. Description of Study

Instruments

CRDS gas analyzer Picarro GT 2401 and chromatograph Agilent 7890B with FID + methanizer were used for analysis.

Calibration Standards

All calibration gas mixtures were prepared gravimetrically according to ISO 6142:2015 by 4 stage dilution of pure carbon monoxide. Purity analysis of CO was carried out by chromatography (Agilent 7890B with TCD) and hygrometry (chilled mirror hygrometer S8000RS “Michell Instruments”). Purity analysis of N\textsubscript{2} was carried out by chromatography (TGA 1326 with PDHID, Agilent 7890B with FID + methanator), electrochemical analyzer Delta F and hygrometry. Verification of all prepared gas mixtures (there were prepared 4 gas mixtures with similar component content) was carried out in accordance with ISO 6143.

Composition of one of calibration standards is shown below

<table>
<thead>
<tr>
<th>Component</th>
<th>Cylinder № D958516</th>
<th>Standard uncertainty u(x)*, μmol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x, μmol/mol</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>5.0006</td>
<td>0.0030</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>balance</td>
<td></td>
</tr>
</tbody>
</table>

* Standard uncertainty u(x) includes uncertainty from gravimetric preparation and uncertainty from verification.

Instrument Calibration

Three independent measurements were carried out under repeatability conditions. Before each measurement an instrument calibration was made. One measurement included 10 sub-measurements.

Sample Handling

The time of the cylinder keeping - 24 hrs.
Input of the sample to the instrument was carried out with the help of automatic unit of commutation.
### Uncertainty

**Uncertainty table: CO**

<table>
<thead>
<tr>
<th>Uncertainty source ( X_j )</th>
<th>Evaluation type</th>
<th>Standard uncertainty ( u(x_j), \mu\text{mol/mol} )</th>
<th>Sensitivity coefficient ( c_j )</th>
<th>Contribution to standard uncertainty ( u_j(y), \mu\text{mol/mol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration gas mixture (gravimetric preparation + verification)</td>
<td>A, B</td>
<td>0.0030</td>
<td>1.004</td>
<td>0.0030</td>
</tr>
<tr>
<td>Analysis (measurements)</td>
<td>A</td>
<td>0.0027</td>
<td>1.000</td>
<td>0.0027</td>
</tr>
<tr>
<td>Combined standard uncertainty</td>
<td></td>
<td></td>
<td></td>
<td>0.0040</td>
</tr>
</tbody>
</table>

Coverage factor: \( k = 2 \)
Expanded uncertainty: 0.008 \( \mu\text{mol/mol} \)