METROLOGICAL ASSURENCE OF O3, CO2, CH4 AND CO CONTROL IN ATMOSPHERE

Leonid A. Konopelko
Yuri A. Kustikov
Vitaly V. Beloborodov
Dmitry N. Selukov

D.I.Mendeleyev Institute for Metrology (VNIIM), 19 Moskovsky ave., 190005, St. Petersburg, Russia
Tel.: +7-812-315-1145, Fax: +7-812- 327-9776, E-mail: lkonop@b10.vniim.ru

Conventional and remote control of ozone, carbon dioxide, methane, and carbon oxide with required accuracy is the primary task for the system of global atmosphere watch. Interest to this task has become stronger lately in connection with global environmental and climate changes and in connection with the fact that many measuring methods do not still provide required accuracy. The problem of global measurement traceability has become very important. Indispensable elements of global measurement traceability are traceability of measurement results of O3, CO2, CH4, and CO analyzers to the national etalon of each country and comparability of national etalons internationally.

Features of traceability for O3, CO2, CH4, CO to national standard and details and results of key comparisons with participation of D.I.Mendeleyev Institute for Metrology (VNIIM) are analyzed for O3, CO2, CH4, and CO species.

Introduction

Requirements to measurement accuracy of gas concentrations have increased for many tasks last years. Particularly it refers to ambient control of ozone and greenhouse gases where there is a need to increase measurement accuracy of the most measurement instruments considerably.
This task has two aspects from metrological point of view:
1. Traceability of results of measurement for O3, CO2, CH4, CO to national standard, which is based on national primary measurement standard and realization of traceability chain from field measuring instrumentation to national standards.
2. Comparability of national standards.
Comparability of national standards is provided by ensuring the equivalence of national standards of countries, which is established by international key comparisons conducted in the frame of Mutual Recognition Arrangement (CIPM MRA) for national measurement standards and for calibration and measurement certificates issued by national metrological institutes under the aegis of the BIPM.
VNIIM has an experience of cooperation with the world metrological centers and participates in the most key comparisons.
The purpose of this work is to show features of traceability for O3, CO2, CH4, CO to national standard and details and results of key comparisons with D.I.Mendeleyev Institute for Metrology (VNIIM).

Traceability ensurence to national standard

National standard of Russia in the field of gas analysis - national primary measurement standard GET-154-09 for the first time was approved in 1980 and since that was upgraded many times and presently includes 19 etalon complexes of calibration and measurement capabilities (CMC), which embrace more than 70 gases and vapors. 315 CMC are placed in the BIPM international database in accordance with Mutual Recognition Arrangement (MRA CIPM) including greenhouse gases. Several physics-chemical methods (GC, gravimetric, photometric, spectrometric, optico-acoustic, fluorescent, chemiluminescent, magnetic-mechanical, interferometric, electrochemical) which provide reproducibility, storage and transference of mole fraction and mass concentration of components in gas media are placed in the base of the national standard. National primary measurement standard GET-154-09 is presented on Fig.1 and state hierarchy verification scheme for the instruments measuring the content of components in the gas media on Fig. 2 [1].

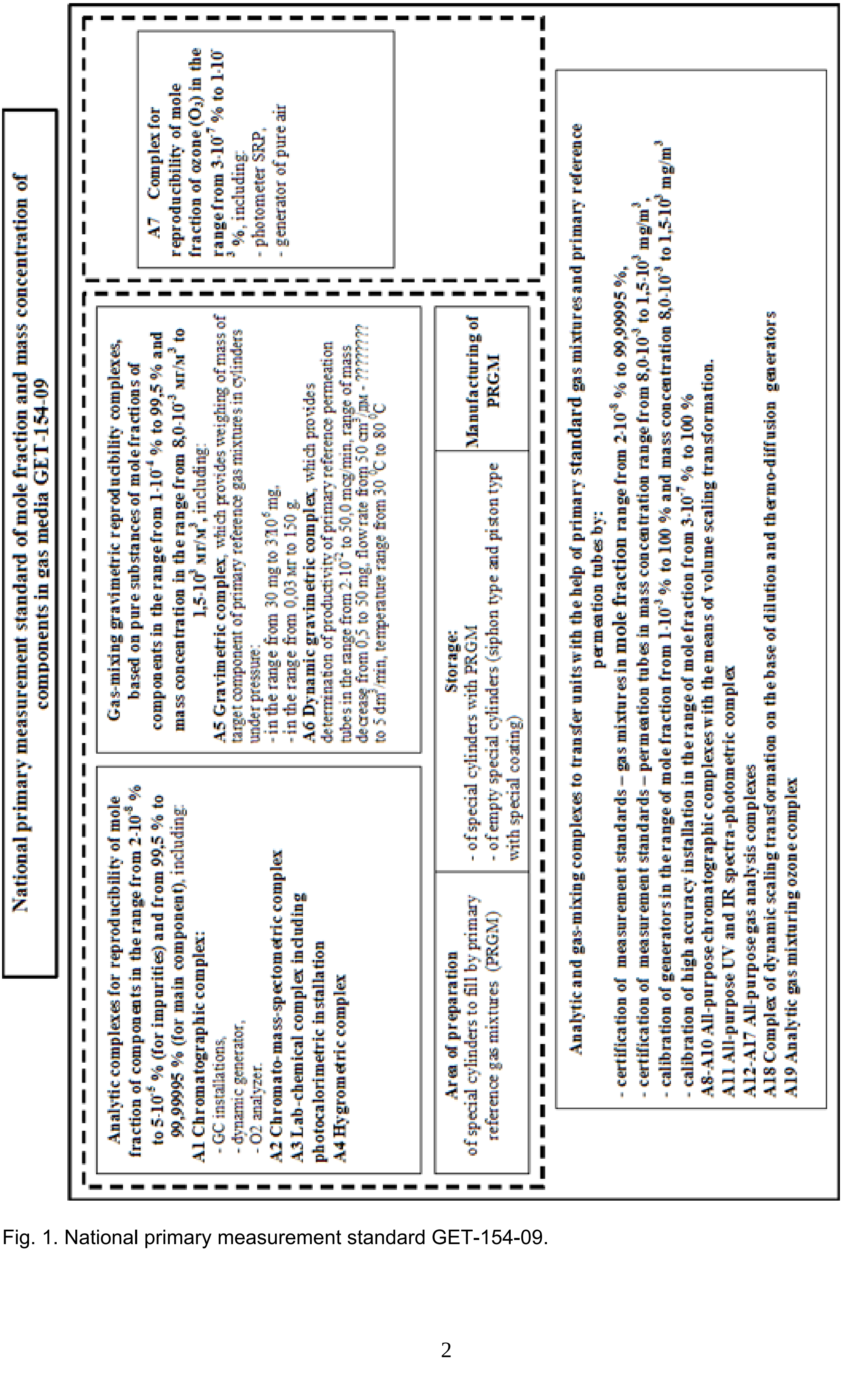

Fig. 1. National primary measurement standard GET-154-09.

State Hierarchy Scheme for the Instruments Measuring the Content of Components in Gas Media

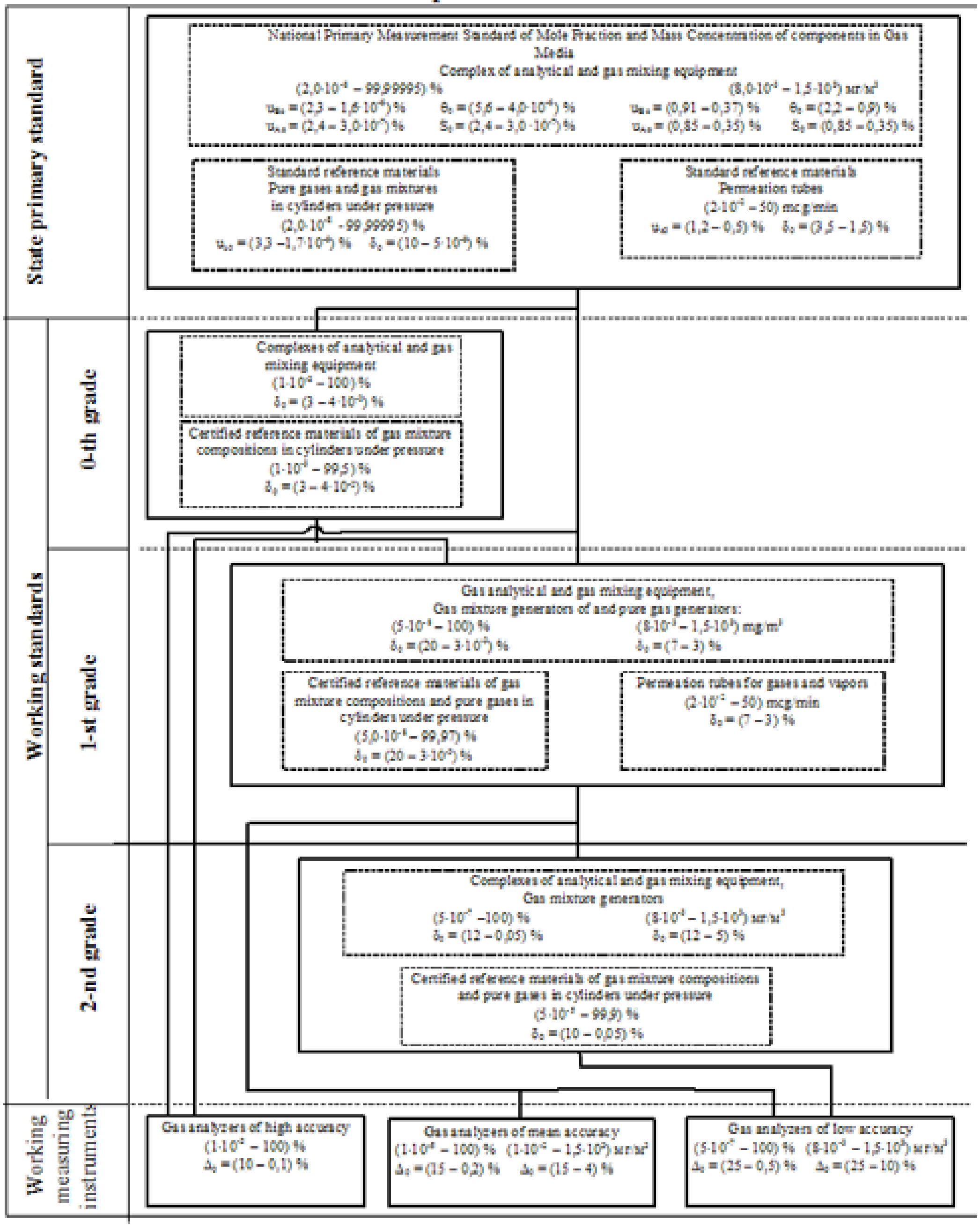

Fig. 2. State Hierarchy Verification Scheme for the Instruments Measuring the Content of Components in the Gas Media [1]

According to Russian legislation, traceability of measurements from working measuring instruments to national primary measurement standard is based on state hierarchy verification scheme for the instruments measuring the content of components in the gas media description of which is presented in GOST 8.578-2008 [1]. This GOST is accepted by 8 NIS countries. This is many level calibration scheme which traceability is provided by working standards of different accuracy and also includes certified reference materials (CRM) – gas mixtures in cylinders under pressure and permeation tubes. GOST 8.578-2008 also has requirements to uncertainties of all components of state hierarchy verification scheme - national primary measurement standard, working standards, and working measuring instruments.
Internationally recognized etalon to measure ozone concentrations is SRP photometer [2, 3] developed in the National Institute of Standards and Technology (USA) included in GET 154-09.

SRP photometer is used in the national primary measurement standards of 17 countries including Russia in the complex for reproducibility of mole fraction of ozone.
Uncertainty budget of the complex for reproducibility of mole fraction of ozone is represented in table 1.

Table 1. Uncertainty budget of the complex for reproducibility of mole fraction of ozone

Component of Uncertainty	Source of Uncertainty	Distribution	Standard Uncertainty	Total Standard Uncertainty	Contribution of Photometer to Total Standard Uncertainty, nmol/mol
Pressure P	Standard uncertainty of pressure sensor	Uniform	0.029 kPa	0.034 kPa	$3.36 \cdot 10^{-4} \cdot x$
	Pressure difference in cells	Uniform	0.017 kPa		
Twemperature T	Pressure sensor error	Uniform	0.087 °C	0.104 °C	$3.52 \cdot 10^{-4} \cdot x$
	Temperature difference in cells	Uniform	0.057 °C		
Optical Path $L_{опт}$	Measurement accuracy	Uniform	0.0046 cm	0.52 cm	$2.89 \cdot 10^{-3} \cdot x$
	Shift	Uniform	0.52 cm		
Intensity Ratio D	Reproducibility	Triangle	$0.98 \cdot 10^{-6}$	$1.06 \cdot 10^{-6}$	0,21
	Resolution	Uniform	$0.41 \cdot 10^{-6}$		
Cross-section		Uniform	$1{,}22 \cdot 10^{-19}$ cm^2	$1{,}22 \cdot 10^{-19}$ cm^2	$1{,}06 \cdot 10^{-2} \cdot x$

Working standards of the 1-st grade and the 2-nd grade are used to provide traceability of field ozone analyzers to the national primary measurement standard GET-154-09. Transportable etalon as a part of the complex for reproducibility of mole fraction of ozone is used to calibrate the 1-st grade ozone generators.
Uncertainty budgets of CO2, CO, and CH4 etalon complexes which are parts of GET 514-09 are presented in tables 2, 3 and 4 correspondently.

Table 2. Uncertainty budget of CO2 etalon complex

№	Source of uncertainty			Type of evaluation	Standard uncertainty, 10^{-6} mol/mol
1	Preparation of standard gas mixtures	Weighing of the pre-mixtures		A	0,061
		Weighing of the final mixtures		A	0,23
		Purity of gases	CO_2 in N_2	A;B	0,010
			CO_2 in O_2	A;B	0,0034
			Other impurities in N_2	A;B	0,00002
			Other impurities in O_2	A;B	0,000008
			Impurities in CO_2	A;B	0,00033
2	Standard deviation of the measurement result			A	0,24
Combined standard uncertainty				0,34	
Expanded uncertainty				0,7	

Table 3. Uncertainty budget of CO etalon complex

№	Source of uncertainty	Type of evaluation	Standard uncertainty, % relative
1	Preparation of the calibration gas mixtures	A, B	0,15
2	Standard uncertainty of calibration	A	0,14
3	Standard deviation of the measurement result	A	0,13
Combined standard uncertainty			**0,24**
Expanded uncertainty (k=2)			**0,48**

Table 4. Uncertainty budget of CH4 etalon complex

№	Source of uncertainty	Type of evaluation	Standard uncertainty, % relative
1	Preparation of the calibration gas mixtures	A, B	0,28
2	Standard uncertainty of calibration	A	0,64
3	Standard deviation of the measurement result	A	0,58
Combined standard uncertainty			0.91
Expanded uncertainty (k=2)			1,82

Comparability assurance to national standard

Ozone

To establish the comparability, key comparisons of national primary measurement standards are conducted periodically by the BIPM (CCQM-P28 in 2005, BIPM.QM-K1 in 2007÷2008). national primary measurement standards are compared to the international standard which is located in the BIPM.

There are two protocols to conduct key comparisons:

- Protocol “A”. Country-participant carries its national etalon to the BIPM where it is compared to the international standard.
- Protocol “B”. Transportable etalon is used. Country-participant compares its transportable etalon to national standard than carries the transportable etalon to the BIPM where it is compared to the international standard. Repeat comparison of the transportable etalon to the national standard to check stability of the transportable etalon is conducted after it comes back to the country-participant.

In accordance with protocol “B” D.I.Mendeleyev Institute for Metrology has participated in key comparison BIPM-QM.K1. Specially selected after investigation of its specifications ozone gas analyzer, type 49i, manufactured by Thermo Electron was used as a transportable etalon.

Degree of equivalence of national etalon to the international standard is established as a result of difference of measurement results conducted by national and international etalons.

$$D = x_{NS} - x_{RS}$$

Degree of equivalence in key comparison BIPM-QM.K1 was estimated for two nominal meanings of ozone mole fractions 80 nmol/mol and 420 nmol/mol [4].

Degree of equivalence of national primary measurement standard GET-154-09 to the BIPM international standard and its expanded uncertainty are presented in table 5.

Table 5. Degree of equivalence of national primary measurement standard GET-154-09 to the BIPM international standard

Nominal meaning	Degree of equivalence D_i, nmol/mol	Standard uncertainty of degree of equivalence $u(D_i)$, nmol/mol	Expanded uncertainty of degree of equivalence $U(D_i)$, nmol/mol
80	-0.28	0.43	0.86
420	-1.47	1.75	3.50
80	-0.22	0.43	0.87
420	-1.82	1.79	3.58

Degree of equivalence of national primary measurement standards of participating in key comparison BIPM-QM.K1 institutes [4], are presented on Fig. 3.

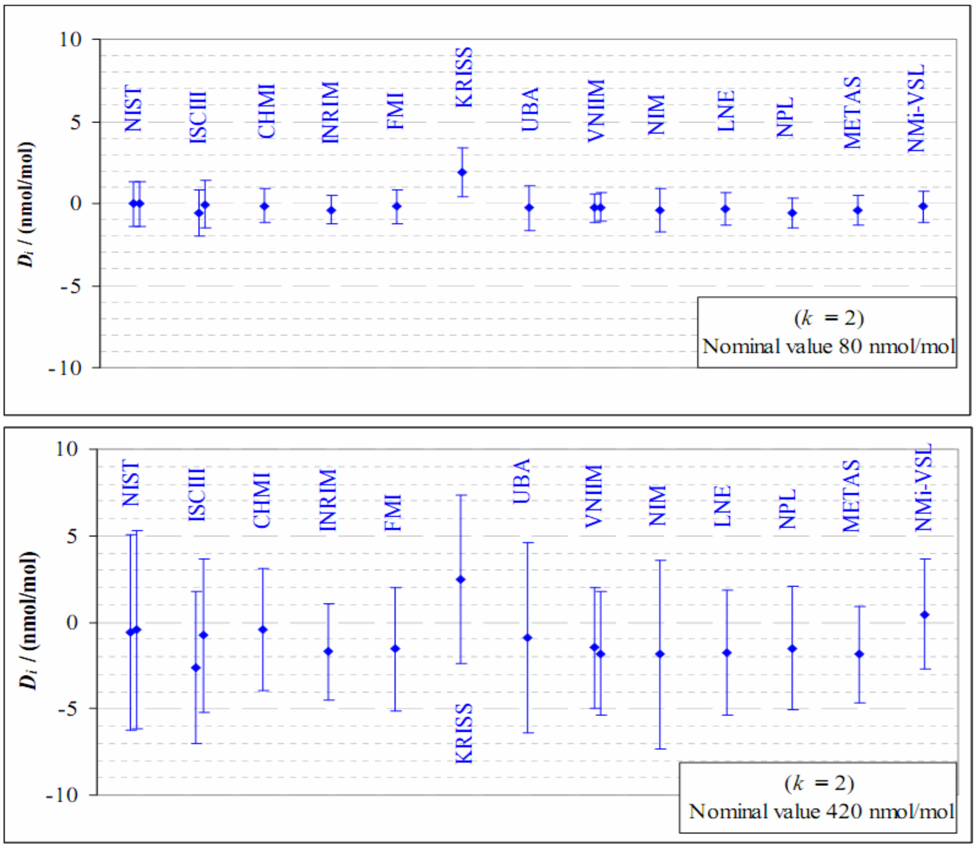

Fig. 3. Degree of equivalence of national primary measurement standards of participating in key comparison BIPM-QM.K1 institutes

Carbon dioxide, carbon oxide, and methane

Key comparison CCQM-P41 (greenhouse gases) [5] between National Metrology Institutes and institutes of World Meteorology Organization which has shown good conformity of results was organized already in 2003 – Fig. 4.

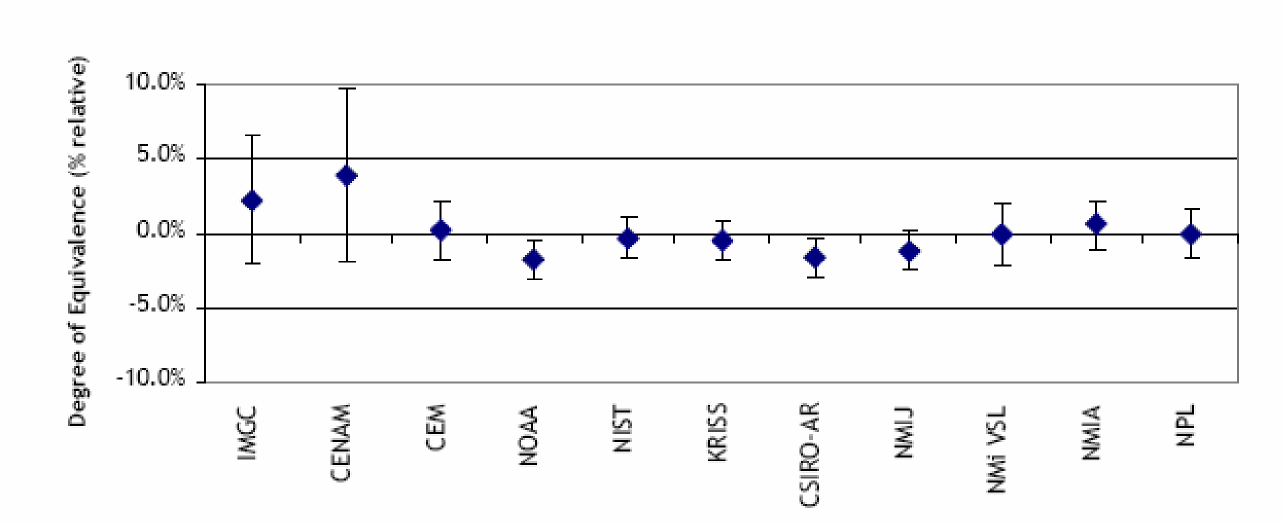

Fig. 4. Degree of equivalence of national primary measurement standards of participating in key comparison CCQM-P41 institutes for CH4 [5]

It was proposed on the meeting of gas analysis working group in 2005 to repeat key comparisons for stable gas mixtures each 10 years and so International Comparison CCQM K52 – Carbon dioxide in Synthetic Air was organized [6].
Concentration of CO2 (360 µmol/mol) approximately corresponds to concentration of CO2 in atmosphere. CO2 gas mixtures were prepared gravimetrically in the Netherland Metrology Institute (VSL) and were calibrated by national primary measurement standard of VSL. CO2 concentrations were prepared gravimetrically and by investigation of pureness of gases present in gas mixture. Each laboratory had to conduct at least 3 measurements in the terms of repeatability with a calibration for each measurement.
Three sources of gravimetric preparation were examined:

1. Gravimetric preparation
2. Purity of the parent gases
3. Stability of the gas mixture

GC and NDIR (used by VNIIM) methods were used by laboratories. 18 national metrology institutes participated in CCQM K52.
25 national metrology institutes participated in the key comparisons CCQM-K51 Carbon monoxide (CO) in nitrogen (5 µmol/mol) [7]. Concentration 5 µmol/mol of CO can be in atmosphere.
Different measurement methods were used by different laboratories – GC (used by VNIIM), gas-filter correlation spectroscopy, NDIR, and FTIR.
The combined standard uncertainty of a reference value $u_{i,ref}$ (for a mixture *i*) was calculated on the base of the following equation:

$$u_{i,ref}^2 = u_{i,grav}^2 + u_{i,ver}^2 + u_{i,stab}^2 \qquad (1)$$

where
$u_{i,grav}$ - standard uncertainty of gravimetric preparation

$$u_{i,grav}^2 = u_{i,weighing}^2 + u_{i,purity}^2 \qquad (2)$$

$u_{i,weighing}$ - standard uncertainty of weighing process;
$u_{i,purity}$ - standard uncertainty due to the purity of the parent gases/liquids;
$u_{i,ver}$ - standard uncertainty from verification;
$u_{i,stab}$ - standard uncertainty due to instability.

There has been no evidence that there would be relevant effect of adsorption.

Long-term stability measurements (during a year) did not show any change in the concentration of the target components within accuracy of these measurements, so that there was not any corrections due to instability.
The standard uncertainty due to instability was taken as zero $u_{i,stab} = 0$.

The expression for the combined standard uncertainty of a reference value becomes thus:

$$u^2_{i,ref} = u^2_{i,grav} + u^2_{i,ver} \quad (3)$$

The degree of equivalence (unilateral) D_i for each participating laboratory in a key comparison is defined in accordance with the equation:

$$D_i = x_{i,lab} - x_{KCRV} \quad (4)$$

Since the comparison gas mixtures had (slightly) different concentrations and taking into account the fact, that the pilot 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:

$$D_i = x_{i,lab} - x_{i,,ref} \quad (5)$$

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

$$u(D_i) = \sqrt{u^2_{i,lab} + u^2_{i,grav} + u^2_{i,ver}} \quad (6)$$

The expanded uncertainty $U(D_i)$ at a 95 % confidence level

$$U(D_i) = k\sqrt{u^2_{i,lab} + u^2_{i,grav} + u^2_{i,ver}} \quad (7)$$

Where k is a coverage factor, k=2

Results of CO2 key comparisons of VNIIM are presented in table 6 [6].

Table 6. Results of CO2 key comparisons of VNIIM

Laboratory code	Cylinder	*xprep uprep uver uref*	*xlab Ulab klab*	*Δx k U(Δx)*
VNIIM	D751937	364.19 0.073 0.18 0.20	364.1 0.7 2	-0.09 2 0.8

In table 6 uncertainties are shown for 95% confidence interval. Evaluation of the degree of equivalence was made with assumption of normal distribution. To get the standard uncertainty of laboratory result the expanded uncertainty was divided on coverage factor k=2.

Results of CO key comparisons of VNIIM are presented in table 7 [7].

Table 7. Results of CO key comparisons of VNIIM

Laboratory code	Cylinder	*xprep uprep uver uref*	*xlab Ulab klab*	*Δx k U(Δx)*
VNIIM	M55 5669	5.0195 0.0030 0.0100 0.0104	5.0410 0.0240 2	0.0215 2 0.0318

Degrees of equivalence of CO2 national primary measurement standards of participating in key comparison CCQM-K52 [6] institutes are presented on Fig. 5 and degrees of equivalence of CO national primary measurement standards for institutes participated in CCQM-K51 [7] are presented on Fig. 6.

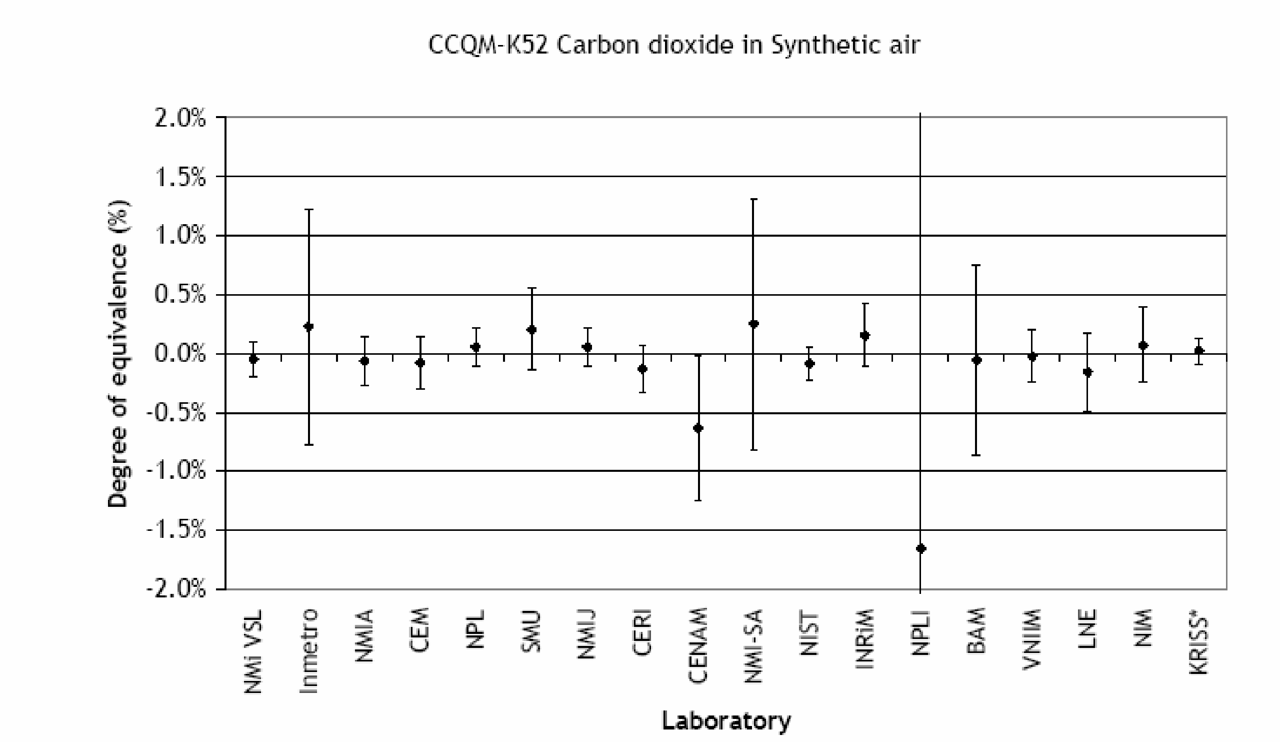

Fig. 5. Degrees of equivalence of CO2 national primary measurement standards of participating in key comparison CCQM-K52 [6] institutes

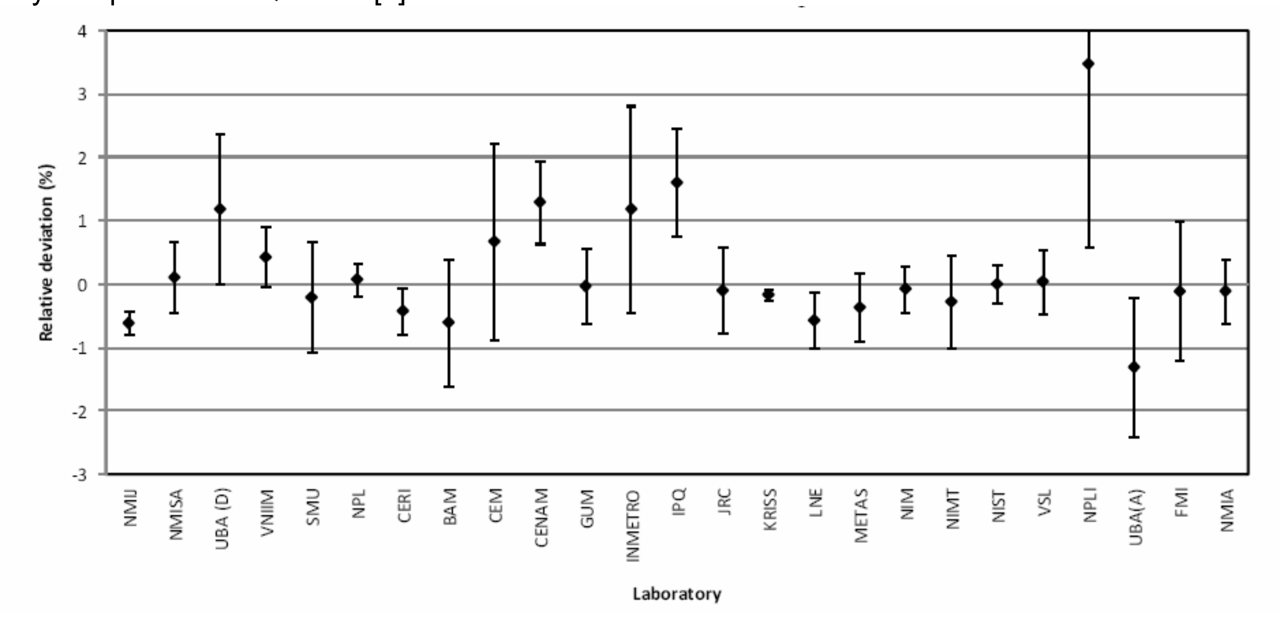

Fig. 6. Degrees of equivalence of CO national primary measurement standards of participating in key comparison CCQM-K51 [7] institutes

Conclusion

Considerable improvement of accuracy of O3, CO2, CH4, CO measurement is impossible without measures one of which is key comparisons with the use of experience of national metrology institutes and working out the measurement procedures.

It is very important to apply cumulative experience/methods/procedures in conducting mutual activity with WMO for which there are good perspectives after signing several agreements by BIPM and by WMO. On April 1, 2010 the WMO acceded to MRA CIPM.

The results of international key comparisons has approved specifications of national primary measurement standard GET-154-09 of VNIIM that made it possible for declared by Russia calibration and measurement capabilities in the field of gas analysis of many gas components to pass international expertise and to get recommendation of the Consultative Committee for Amount of Substance (CCQM) to be included to the international database of BIPM [http://kcdb.bipm.org/appendixC].

Literature

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