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REFERENCE MATERIALS IN MEASUREMENT AND TECHNOLOGY

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The Conference proceedings contains materials on general theoretical, metrological and practical issues of the creation, application of reference materials. The materials provided by the authors is not reviewed. The authors bear full responsibility for the authenticity and accuracy of citation, names, titles etc., as well as compliance with intellectual property law.

Dear Colleagues!

Under the authority of Programme and Organizing Committee of the IVth International Scientific Conference "Reference Materials in Measurement and Technology" we would like to welcome each of you and express our gratitude for your participation.

This year made major changes in the work of most companies around the world. Our conference was not an exception. But we were able to adapt the format of our forum to the current realities. We promise to make every effort to ensure that the experience of using the opportunities of online platforms in the conference is successful, and we sincerely wish all participants to make the most of it for their research activities.

Measurement accuracy at the moment is critical in all industries and life-support areas. Quality control and product safety is especially important in the field of medicine and clinical diagnostic research, in innovative high-tech sectors. Institutes-developers and producers of reference materials are receiving increasing in volume and complexity requests to which metrological community has learned to find a joint effective response.

We are glad that the Conference was able to become an authoritative platform that brings together leading experts in various fields of measurement, successful developers of reference materials for the composition and properties of substances and materials from Russia, CIS countries and Europe.

The programme of the Conference in 2020 includes next discussions:

- Theory and practice of development, production, distribution and implementation of Reference Materials;
- Metrological Assurance with application of Reference Materials in various economical fields;
- Primary reference measurement procedures and reference measurement procedures;
- Interlaboratory comparison;
- International cooperation in the field of RMs;
- Reference Materials in legal metrology;

The participants are faced with the task of developing and releasing competitive technological solutions to the market in a short time, ensuring their application with standards and methods, as well as a regulatory framework. Discussion and refinement of roadmaps for the development of" end-to-end" digital technologies prepared by the Russian expert community will be an important part of the conference.

Organizers of the Conference wish all of participants a good mood and also successful and productively work!

CONTENT

GRADUATION OF AMR-1006M NMR ANALYZERS USING NATURAL SAMPLES AND SAMPLES-IMITATORS

Oleg S. Agafonov, Sergey M. Prudnikov

Federal state budgetary scientific institution «Federal scientific center
«V.S. Pustovoit All-Russian Research Institute of Oil crops», Krasnodar, Russia
ORCID 0000-0002-0209-5432, e-mail: sacred_jktu@bk.ru

Key words: sunflower seeds, mass fraction of oleic acid, nuclear magnetic decompression, standard imitating samples, express method

The derivation of new types of raw materials, in particular, high oleic sunflower seeds [1], posed the urgent task of controlling the content of oleic acid in seed oil for the enterprises of the oil and fat industry. At present, this indicator is not regulated by state standards, but is set by enterprises independently in the form of a minimum base value (usually 78 - 85%).

The fatty acid composition of sunflower seed oil is influenced by various factors: species characteristics, agroclimatic conditions, as well as seed cultivation technologies [2, 3]. It is also possible to deliberately falsify lots of high oleic sunflower seeds (in view of the higher cost of such raw materials).

We have developed an instrumental method for determining the mass fraction of oleic acid in sunflower seed oil [4] using the pulse NMR method. The proposed method compares favorably with the existing ones: efficiency (analysis time of one sample is less than 1 minute), lack of complex sample preparation, high representativeness, and the possibility of simultaneous determination of several indicators.

For the effective implementation of this method at the enterprises of the fat-and-oil industry, it is necessary to develop an effective calibration and verification system for NMR analyzers AMV-1006M. To solve this problem, we have developed a special set of CO-simulators of various mass fractions of oleic acid in sunflower seed oil based on chemically inert substances [5].

The purpose of this work is to study the influence of the samples used on the results of the calibration of NMR analyzers when determining the mass fraction of oleic acid in sunflower seed oil. Based on this task, natural samples of sunflower seeds were prepared with a mass fraction of oleic acid in seed oil in the range from 31% to 86%, as well as a set of CO-simulators, with certified values of the mass fraction of oleic acid in the range from 31 to 93%.

Table 1. Evaluation of metrological characteristics when calibrating NMR analyzer AMV-1006M

Meterange	**The measured value of the mass fraction of oleic acid,%**			
	CO simulators		**Seed**	
	31	**81**	**31**	**79**
1	30	80	30	77
2	30	80	29	75
3	31	80	31	78
4	30	82	34	79
5	30	80	28	77
6	32	81	32	76
7	31	82	32	79
8	30	80	30	76
9	31	82	35	82
10	32	81	36	81
11	31	81	35	78
12	32	80	34	83
$\overline{x}$	**30,83**	**80,75**	**32,17**	**78,42**
$S_{\overline{x}}$	**0,25**	**0,26**	**0,79**	**0,75**
ε	**0,57**	**0,59**	**1,79**	**1,71**

During the measurements, the samples were kept at the required temperature for 2 hours, and their NMR relaxation characteristics were measured on an AMV-1006M NMR analyzer.

Table 1 shows the results of measurements of CO-simulators and sunflower seeds with various certified values of the mass fraction of oleic acid, executed in 12 replicates on an AMR-1006M NMR analyzer.

The data in table 1 show that the relative standard deviations of the measurement results (Sx) and the boundaries of the confidence random error of the measurement results (ε) when using CO-simulators is 3 times lower compared to the results of measurements obtained using natural sunflower seeds.

To check the reproducibility of the calibration results using CO simulators and sunflower seed samples, four AMV-1006M NMR analyzers were used, which were in the same operating conditions to exclude the effect of temperature on the calibration results (Table 2 and 3).

Table 2. Measurement results when calibrating NMR analyzers using CO simulators of the mass fraction of oleic acid

Sample	**Certified value,%**	**The results of measurements of ppm oleic acid, obtained on the device,%**				$S_{\bar{x}}$	ε
		1	**2**	**3**	**4**		
1	31	30	31	31	32	**0,41**	**1,30**
2	52	52	53	53	51	**0,48**	**1,52**
3	62	62	63	62	61	**0,41**	**1,30**
4	73	72	74	73	73	**0,41**	**1,30**
5	81	82	80	80	81	**0,48**	**1,52**
6	93	94	93	92	94	**0,48**	**1,52**

Table 3. Measurement results obtained when calibrating NMR analyzers using natural sunflower seeds

Sample	**Certified value,%**	**The results of measurements of ppm oleic acid, obtained on the device,%**				$S_{\bar{x}}$	ε
		1	**2**	**3**	**4**		
1	31	28	32	32	33	**1,11**	**3,53**
2	48	46	45	46	47	**0,41**	**1,30**
3	69	70	65	72	71	**1,55**	**4,94**
4	72	76	73	73	70	**1,22**	**3,89**
5	79	76	82	80	80	**1,26**	**4,00**
6	86	83	85	83	86	**0,75**	**2,39**

From the data in table 2 and 3, it means that the results of the reproducibility of the calibration of NMR analyzers using CO simulators of the mass fraction of oleic acid are better than those when using sunflower seeds. This is due to the fact that CO-simulators have a fairly homogeneous structure, which is formed during their manufacture. Sunflower seeds are a complex heterogeneous system with a heterogeneous structure in the analyzed volume.

Studies of the effect of temperature on the results of the calibration of NMR analyzers using CO-simulators and natural seed samples also showed the superiority of the former in metrological characteristics. The data obtained show that seeds are more influenced by temperature than CO-simulators of the mass fraction of oleic acid. So the standard deviation for CO-simulators does not exceed 0.8%, while for seeds the values of 2.5% were obtained. This nature of the effect of temperature can be explained by the fact that temperature affects to a lesser extent the mobility of protons contained in imitating substances than in natural seeds.

The results of the studies have shown the expediency of using special CO-simulators for the calibration of AMV-1006M NMR analyzers in comparison with natural seed samples. The use of

CO-simulators of the mass fraction of oleic acid in sunflower seed oil makes it possible to improve the repeatability and reproducibility of calibration results by almost two times. The developed CO-simulators are less susceptible to the influence of temperature, have a higher stability of their physicochemical parameters, and, consequently, of the certified values.

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NON-CONFORMITIES OF PROVISIONS OF REFERENCE MATERIAL REGULATORY DOCUMENTS

Elena Anchutina

Joint Stock Company “Ekaterinburg Non-Ferrous Metals Processing Plant” (EZOCM),
Verkhnyaya Pyshma, Russia, e-mail: lanchut@yandex.ru

Key words: ISO standards, ISO Guides, standard sample, reference material, reference material certification, certified reference material, reference material production

Currently, there is only one international standard in the field of reference materials (RMs) – ISO 17034: 2016 [1] setting the requirements for the competence of RM producers. While the implementation period for this standard has ended in November 2019, a Russian-language version of this standard has not yet appeared in Russia. Moreover, the Russian standard GOST ISO Guide 34-2014 [2] is still valid, though the ISO Guide 34 was canceled due to the release of the ISO 17034:2016 standard.

Two translations of the ISO 17034: 2016 standard into Russian are issued – one of them was made by the Ural Research Institute of Metrology and released by publishing house "Standartinform" [3], the other was fulfilled by the accreditation body “Association of Analytical Centers "Analytica" [4] and posted on this accreditation body website. Obviously, that the translation is not a normative document, it does not go through the review and approval as to draft standards, and it can only be used as a reference material.

Nevertheless, several standards [2, 5-11] developed as identical international documents in the field of reference materials or harmonized with them were introduced in Russia. The presentation considers the non-conformities of some provisions of these standards with the requirements of regulatory legal acts, other Russian standards and international documents, and ways to eliminate these non-conformities are proposed.

Elimination of non-conformities will help to introduce the international requirements concerning to reference materials into the Russian system of metrological ensuring the measurements and to apply them correctly.

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DEVELOPMENT OF REFERENCE MATERIALS FOR GAS PERMEABILITY

Iliya P. Aronov, Egor P. Sobina

UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
e-mail: ilusa090695@mail.ru

Keywords: oil industry, reference material, gas permeability coefficient, absolute gas permeability coefficient, stationary filtration method, Darcy Law, Klinkenberg effect

Metrological support of measurements in the field of extractive industry in Russia is one of the main directions providing obtaining reliable results of measurements during oil and gas production. The most important measured physical value of these industries is the permeability of rocks. Permeability is being analyzed by almost all core laboratories, and its measurements are included in the list of mandatory ones [1]. Permeability is the property of rocks to transmit liquids, gases and their mixtures in the presence of a pressure gradient [2]. This parameter allows estimating both recoverable hydrocarbon reserves and oil and gas production technologies, as well as flow rates and productivity of wells. A distinction is made between absolute, effective and relative permeability. Absolute permeability is used for general characterization of physical properties of rocks, which is generally understood as permeability of porous medium, which is defined when there is one phase, chemically inert to the rock. To determine the absolute permeability, air or gas (usually helium and nitrogen) is often used. As a result, there is such a measurable value as gas permeability (also called gas permeability coefficient) - the property of the rock to transmit gases in the presence of a pressure drop due to the intercommunicability of voids (pores, channels, cracks). The gas permeability is measured according to GOST 26450.2-85 [3] on instruments implementing the stationary and non-stationary filtration method. In this work stationary filtration method is used, as it directly implements the Darcy filtration law. The value unit of gas permeability coefficient is [m^2].

The analysis of the Federal Information Fund on Ensuring Uniformity of Measurements has shown that all existing reference materials (hereinafter referred to as RM) of rock gas permeability in Russia have been certified by means of interlaboratory experiment, which does not provide direct traceability to the State primary standards, but only to the calibrated rock gas permeability analyzers, which are calibrated using the same RM. As a result, in metrological practice for RM permeability of rocks there is no stable in time basis for comparison. This fact justifies the relevance of this work, which resulted in the development of a set of RM gas permeability of rocks, certified values of which were obtained directly with the help of GET 210-2019 - State primary standard of units of specific adsorption of gases, specific surface, specific volume of pores, pore size, open porosity and coefficient of gas permeability of solids and materials.

Fig. 1 - Appearance of RM gas permeability

Ceramic cylinders (material - molded corundum sintered refractory, Al_2O_3 content more than 90%), 30 mm in diameter and 30 mm in height (figure 1) were chosen as the starting material for RM. This material sufficiently simulates the real core, while having greater strength and stability. Another important factor in the choice was the fact that the manufacturer of this material has the technological ability to regulate the porosity and permeability of the final product, which allowed to create RM, covering the entire required measuring range (0,1·10-3 - 5 μm^2).

RM certified characteristics are gas permeability coefficients at given reciprocal pore pressures (2, 3...8 MPa^{-1}) for helium and nitrogen as well as absolute gas permeability coefficient.

The reciprocal pore pressure is calculated by a formula:

$$\frac{1}{p_{por}} = \frac{2}{(p_1 + p_2)}, \qquad (1)$$

where p_1 is the pressure under the sample, MPa; p_2 is the pressure above the sample, MPa.

The certified value of the gas permeability coefficient (10^{-3} μm^2) at a given reciprocal pore pressure is calculated according to the measurement equation obtained from the Darcy law:

$$K = \frac{4000}{3} \cdot \frac{Q \cdot C \cdot l \cdot \mu \cdot p_0}{\pi \cdot d^2 \cdot (p_2^2 - p_1^2)} \cdot \frac{T}{T_0}, \qquad (2)$$

where Q is the volume flow rate of gas reduced to normal conditions (p_0=1,01325 bar and T_0= 273,15 K), dm^3/min; C is the coefficient for correction for thermal conductivity of the gas, l is the length of the sample, mm; μ is the gas viscosity, μPa·s; p_0 - normal pressure, 1,01325 bar; d - sample diameter, mm; p_2 - pressure above sample, bar; p_1 - pressure under sample, bar; T - gas temperature at measurement, K; T_0 - normal temperature, 273,15 K.

The certified value of the absolute gas permeability coefficient is calculated by the following formula:

$$K_{abs} = \frac{K_{abs_{He}} + K_{abs_{N_2}}}{2}, \qquad (3)$$

where $K_{abs_{N2}}$ and $K_{abs_{He}}$ - are the absolute gas permeability coefficients for nitrogen and helium respectively, 10^{-3} μm^2, each of which is calculated separately with regard to the Klinkenberg effect (4) by constructing a linear regression dependence of the gas permeability coefficient on the reverse pore pressure $K = f\left(1/P_{por}\right)$ and extrapolating this dependence to point $1/P_{por} = 0$. The value of the gas permeability coefficient at a given point is equal to the value of the absolute gas permeability coefficient for nitrogen or helium (fig. 2).

$$K = K_{abs} \cdot \left(\frac{b}{p_{por}} + 1\right), \qquad (4)$$

where K is the gas permeability coefficient at a given reciprocal pore pressure in helium or nitrogen, 10^{-3} μm^2, K_{abs} is the absolute gas permeability coefficient in helium or nitrogen, 10^{-3} μm^2, b is the Klinkenberg constant, bar.

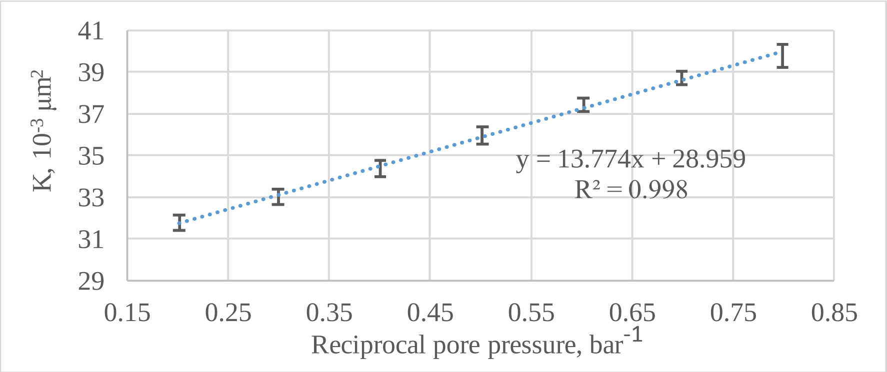

Fig. 2. Dependence of gas permeability coefficient on reciprocal pore pressure. The gas used is helium. In this example, K_{abs} = 28,959 10^{-3} μm^2

Standard uncertainties of the certified values of gas permeability coefficients at the given reciprocal pore pressures were calculated by the formula:

$$u_c = \sqrt{u_{char}^2 + u_{stab}^2}, \qquad (5)$$

where u_{char} is the standard uncertainty of gas permeability coefficient characterization at the given inverse pore pressure, 10^{-3} μm^2;

u_{stab} - standard uncertainty of instability for 2 years, 10^{-3} μm^2;

The standard uncertainty of the certified value of the absolute gas permeability coefficient was calculated by the formula:

$$u_c = \sqrt{\frac{1}{4}(u_{N_2}^2 + u_{He}^2) + u_{stab}^2 + \frac{\Delta^2}{12}}, \qquad (6)$$

where u_{N_2} and u_{He} - standard uncertainties of absolute gas permeability coefficients for nitrogen and helium respectively, 10^{-3} μm^2;

u_{stab} - standard uncertainty of instability for 2 years, 10^{-3} μm^2;

Δ - difference between the values of absolute gas permeability coefficients for nitrogen and helium, 10^{-3} μm^2.

Metrological characteristics of RM rock gas permeability set are presented in table 1, designations *N2* and *He* in the table mean certified values of gas permeability coefficient at the given reciprocal pore pressure ($1/P_{por}$) for nitrogen and helium respectively, 10^{-3} μm^2; K_{abs} - certified value of absolute gas permeability coefficient 10^{-3} μm^2; U_o - relative expanded uncertainty of certified RM value at k=2 and P=0.95%, %.

Table 1. metrological characteristics of RM gas permeability

RM number	GSO 11546-2020			GSO 11547-2020			GSO 11548-2020			GSO 11549-2020			GSO 11550-2020		
$1/P_{por}$, MPa^{-1}	N_2	He	K_{abs}	N_2	He	K_{abs}	N_2	He^2	K_{abs}	N_2	He	K_{abs}	N_2	He	K_{abs}
2	0,6833	0,7474	0,6517	8,310	9,666	7,752	32,05	34,55	30,57	221,1	227,6	219,0	3334	3405	3348
3	0,6963	0,7912		8,621	10,657		32,73	36,96		224,3	232,6		3392	3429	
4	0,7153	0,8449		8,958	11,598		33,44	39,07		225,8	237,7		3413	3454	
5	0,7279	0,8944		9,279	12,550		34,26	41,57		227,4	243,7		3435	3471	
6	0,7376	0,9378		9,617	13,466		34,95	43,87		229,3	248,8		3451	3493	
7	0,7605	0,9038		9,931	14,396		35,58	45,93		231,0	254,0		3463	3514	
8	0,7738	0,8592		10,224	15,283		35,75	48,31		233,0	265,3		3471	3553	
U_o, %	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3

As a result of the work done, a set of gas permeability reference materials GSO 11546-2020/GSO 11550-2020 certified by the State Primary Standard GET 210 was approved, which will ensure metrological traceability and reliability of gas permeability coefficient measurements. RM are designed for certification of measurement methods and control of accuracy of gas permeability coefficient results at the given reciprocal pore pressure on helium and nitrogen and absolute gas permeability coefficient of rocks. Also RM can be used for calibration of measuring instruments, testing of measuring instruments and reference materials for type approval provided that RM complies with the established requirements.

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DEVELOPMENT OF A NEW DATA PROCESSING ALGORITHM FOR MEASURING THE ABSOLUTE GAS PERMEABILITY COEFFICIENT

Peter M. Aronov, Iliya P. Aronov, Egor P. Sobina

UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
e-mail: aronovpm@uniim.ru

Keywords: oil industry, reference material, gas permeability coefficient, absolute gas permeability coefficient, stationary filtration method, Darcy Law, Klinkenberg effect

Permeability of rocks is the property of rocks to transmit liquids, gases and their mixtures in the presence of a pressure gradient [1]. This value is very important for oil industry because it allows estimating oil and gas reserves, as well as development technologies and well productivity. As a general characteristic of physical properties of rocks absolute permeability is used - permeability of porous medium, determined in the presence of one phase, chemically inert with respect to the rock. Air or gas (as a rule, helium and nitrogen) is often used to assess the absolute permeability. Absolute permeability estimated with gas is called the absolute gas permeability coefficient (the unit of magnitude is [m^2]).

For creation of metrological support of absolute gas permeability coefficient measurements UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology (hereinafter UNIIM) has developed a set of reference material for gas permeability of rocks GSO 11546-2020/ GSO 11550-2020, certified with the help of GET 210-2019 - State primary standard of units of specific adsorption of gases, specific surface, specific volume of pores, pore size, open porosity and gas permeability coefficient of solids and materials. The measurement technique applied in establishing the metrological characteristics of reference materials (hereinafter - measurement technique) is based on the method regulated in GOST 26450.2 [2] - namely the method of stationary filtration. The essence of this method is to determine the constant (stationary) rate of gas filtration through the rock sample in a linear direction under the influence of differential pressures. The rate is determined by a known volume of gas passing through the sample over a fixed period of time at a constant pressure differential.

In general, for both gases and liquids, the filtration process is described by the Darcy filtration equation:

$$Q = \frac{K \cdot S \cdot (p_2 - p_1)}{\mu \cdot l}, \qquad (1)$$

where Q is the fluid volume flow rate; S is the cross-sectional area of the sample; K is the permeability factor; p_2 and p_1 are the inlet and outlet pressures respectively; μ is the fluid viscosity; l is the sample length.

Taking into account the technical implementation of measurements on GET 210, equation (1) in expression K, took the form of:

$$K = \frac{4000}{3} \cdot \frac{Q \cdot C \cdot l \cdot \mu \cdot p_0}{\pi \cdot d^2 \cdot (p_2^2 - p_1^2)} \cdot \frac{T}{T_0}, \qquad (2)$$

where Q is the volume flow rate of gas reduced to normal conditions (p_0=1.01325 bar and T_0= 273.15 K), dm^3/min; C is the coefficient for correction for thermal conductivity of the gas, l is the length of the sample, mm; μ is the gas viscosity, μPa·s; p_0 - normal pressure, 1,01325 bar; d - sample diameter, mm; p_2 - sample inlet pressure, bar; p_1 - sample outlet pressure, bar; T - gas temperature at measurement, K; T_0 - normal temperature, 273,15 K.

When measuring gas permeability, there is a deviation from the Darcy law. The cause of deviation is the effect of gas sliding - the Klinkenberg effect [3]. This effect is manifested by the dependence of the measured and calculated according to Darcy law permeability on the pore pressure

$p_{por} = \frac{(p_2 + p_1)}{2}$ in the sample. Permeability measured at pore pressure close to reservoir pressure $p_{por} \rightarrow p_{res}$ is absolute (K_{abs}) and close to liquid permeability that does not react with the rock. The value of absolute gas permeability K_{abs} is related to the value of permeability measured at a given pore pressure, the ratio

$$K_{abs} = \frac{K}{1 + b / P_{por}}, \tag{3}$$

where K_{abs} is the absolute gas permeability coefficient; K is the gas permeability coefficient at a given pore pressure; b is the Klinkenberg coefficient, depending on the rock type and gas filtered.

According to the measurement procedure on GET 210, as well as GOST 26450.2, K_{abs} is determined by measuring and calculating by the formula (2) gas permeability coefficients at several values of pore pressure and constructing a linear regression dependence of gas permeability coefficient on the reciprocal pore pressure $K = f\left(1 / p_{por}\right)$, and extrapolating this dependence to point $1 / P_{por} = 0$.

In most cases, the algorithm for calculating K_{abs} used in the measurement technique on GET 210 is effective and allows to determine K_{abs} with the necessary accuracy (Fig. 1). However, in practice of measurements of this value on different samples there are cases when it is impossible to determine K_{abs} with the necessary accuracy, due to the low value of approximation reliability R^2 (hereinafter R^2) of the dependence of gas permeability coefficient on the reciprocal pore pressure (3). Example - Fig. 2. In accordance with GOST 26450.2 it is necessary to select points for approximation, which are subject to linear model. However, if you look at the experimental data (figure 2), the choice of these points is difficult, and may be ambiguous, and depending on the human factor may lead to significantly different measurement results. It should be noted that there is no strict mathematical criterion for the selection of points when constructing a linear model in the coordinates of Klinkenberg equation in GOST 26450.2.

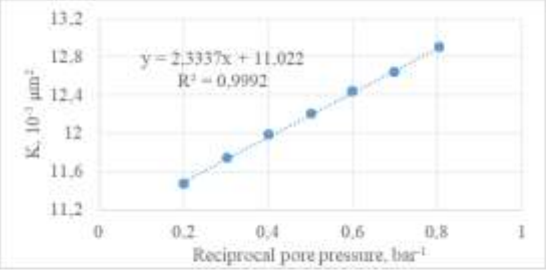

Fig. 1. Dependence of gas permeability coefficient on reciprocal pore pressure

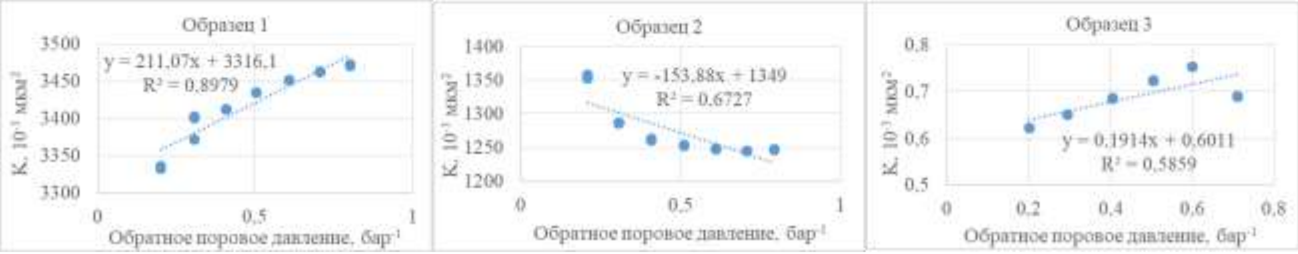

Fig. 2. Dependence of gas permeability coefficient on the inverse pore pressure, having low values of R^2

The graph for the sample 2 in Figure 2 particularly clearly demonstrates the absence of linear dependence of the gas permeability coefficient on the reciprocal pore pressure.

To solve this UNIIM proposed a new algorithm for data processing when measuring the absolute gas permeability coefficient, based on the same laws - the Darcy law (2) and the

Klinkenberg effect (3), as well as the algorithm used in the methods of measurements on GET 210 and GOST 26450.2.

Let us consider the measurement equation of gas permeability coefficient at a given value of pore pressure (2). In this equation we enter $Z = \frac{4000}{3} \cdot \frac{\cdot C \cdot l \cdot \mu \cdot p_0}{\pi \cdot d^2 \cdot} \cdot \frac{T}{T_0}$ for convenience, then:

$$Q = \frac{K \cdot (p_2^2 - p_1^2)}{Z} \tag{4}$$

By dividing both parts of equation (4) by $2 \cdot (p_2 - p_1)$ and multiplied by *Z*, we get:

$$\frac{Q \cdot Z}{2 \cdot (p_2 - p_1)} = K \cdot \frac{(p_2 + p_1)}{2}, \tag{5}$$

where $p_{por} = \frac{(p_2 + p_1)}{2}$ - pore pressure. By substituting equation (5), equation (3) is obtained:

$$\frac{Q \cdot Z}{2 \cdot (p_2 - p_1)} = K_{abs} \cdot \left(b + p_{por}\right) \tag{6}$$

If we denote for $F = \frac{Q \cdot Z}{2 \cdot (p_2 - p_1)}$ and analyze the dimension of this expression, then we come to the fact that F has a unit of force [N]:

$$F = \frac{Q \cdot Z}{2(p_2 - p_1)} = \frac{\frac{[dm^3]}{[s]} \cdot [mm] \cdot [\mu Pa] \cdot [s] \cdot [bar] \cdot [K]}{[bar] \cdot [mm^2] \cdot [K]} = 10^{-6}[m^2] \cdot [Pa] = 10^{-6}[N] \tag{7}$$

This force is a linear pore pressure function:

$$F = K_{abs} \cdot \left(b + P_{por}\right) \tag{8}$$

Let's plot the dependence of *F* on pore pressure $F = f\left(p_{por}\right)$ using the same input data as the diagrams in Fig. 2 and compare them (Fig. 3).

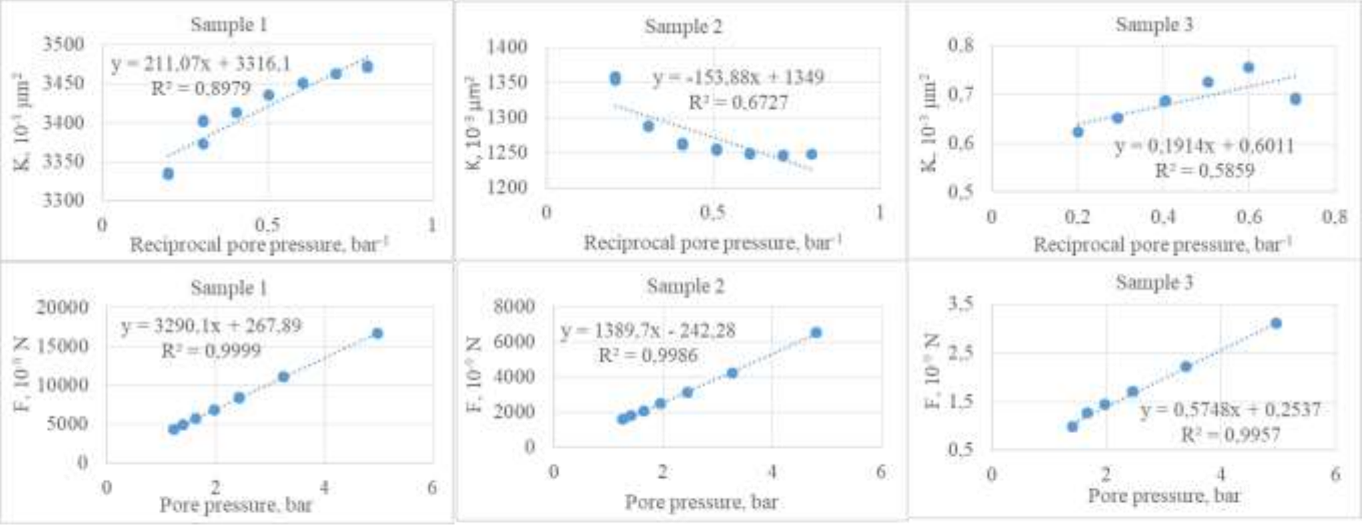

Fig. 3.Results of measurements of absolute gas permeability coefficient obtained by the method of measurements on GET 210 (based on GOST 26540.2-85) - upper row; using the new algorithm proposed in this paper - lower row.

According to figure 3:

- for the sample1: K_{abs}=3316·10^{-3} μm^2, R^2=0,8979 according to the measuring technique on GET 210 (based on GOST 26540.2-85) and K_{abs}=3290·10^{-3} μm^2, R^2=0,9999 according to the new algorithm;
- for the sample 2: K_{abs}=1349·10^{-3} μm^2, R^2=0,6727 according to the measuring technique on GET 210 (based on GOST 26540.2-85) and K_{abs}=1390·10^{-3} μm^2, R^2=0,9986 according to the new algorithm;
- for the sample 3: K_{abs}=0,6011·10^{-3} μm^2, R^2=0,5859 according to the measuring technique on GET 210 (based on GOST 26540.2-85) and K_{abs}=0,5748·10^{-3} μm^2, R^2=0,9957 according to the new algorithm.

We can see that all R^2 samples are higher using the new algorithm.

As a result of this work, a new algorithm for data processing in measuring the absolute permeability coefficient has been developed, which allows to calculate the absolute gas permeability coefficient even in the case when low values of the correlation coefficient in the Klinkenberg equation are observed in the traditional model based on GOST 26450.2. The developed algorithm does not require arbitrary selection of points in the Klinkenberg equation, because when measuring the gas permeability coefficient by the new equation (8) all points are well subdivided. We would like to emphasize separately that the developed model (8) lacks square terms of pressure, all input values are in the first degree, which, in our opinion, provides a higher adequacy of the proposed measurement equation (8). The algorithm proposed in this paper requires additional experimental and theoretical studies and a set of representative sampling results at various points of the measuring range of the gas permeability coefficient, but this work has already obviously demonstrated the prospects of introducing into practice a new algorithm for processing measuring information to determine the absolute gas permeability coefficient.

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IMPLEMENTATION OF THE NEEDS OF THE ENTERPRISE IN INTERLABORATORY RELATIVE TESTS THROUGH ACCREDITED PROVIDERS. FEDERAL ACCREDITATION SERVICE POLICY REGARDING QUALIFICATION VERIFICATION BY INTERLABORATORY DISTANCE TESTING. PLATFORM FOR VERIFICATION OF LABORATORIES 'QUALIFICATIONS

Anton V. Belov

State Regional Centre for Standardization, Metrology and Testing in the Rostov Region (Rostov CSM),
Rostov-on-Don, Russian, e-mail: belov85@inbox.ru

Keywords: interlaboratory comparison tests, competence assessment, metrology, ensuring traceability of measurements, quantitative chemical analysis, provider, accreditation, federal service for accreditation, laboratory proficiency testing platform, reference standard

Interlaboratory comparison testing (ICT) is the organization, conduct and evaluation of tests (measurements, studies) of the same or similar elements by two or more laboratories in accordance with predetermined criteria.

For more than ten years, FBI “Rostov CSM” has been the interlaboratory comparison tests Provider (ICT) in the field of food products, food raw materials, environmental objects, metals and alloys, nanoobjects and nanomaterials. In 2015, it became the first interlaboratory comparison tests Provider [1], which successfully passed the accreditation procedure in the national accreditation system in accordance with the requirements of the Accreditation Criteria (Order of the Ministry of Economic Development of the Russian Federation No. 326 of 30 May 2014) and received the accreditation certificate №. RA.RU.10РД01 of 04.09.2015 that allowed organizing and making interlaboratory comparisons both in the field of quantitative chemical analysis (QCA) and in a completely new and much-in-demand area of ensuring traceability of measurements (verification / calibration of MI).

Interlaboratory comparison tests are organized with the purpose of:

- optimization of procedures for accreditation or confirmation of the competence of accredited (accredited) laboratories by using the results obtained during the ICT
- assessment of characteristics of the test method, as well as interlaboratory certification of the test procedure (measurements);
- assessment of characteristics of a reference standard, as well as interlaboratory certification of the sample for control
- compliance with the policy of the Federal Accreditation Service regarding proficiency testing by conducting an ISI

As a sample for control (SC) for comparisons to ensure traceability of measurements we take a measuring instrument (MI) that must have a valid verification certificate (calibration certificate), be stable (maintain its metrological characteristics throughout the test period). When making comparisons with respect to the quantitative chemical analysis, as SC we take samples having the rank of SRS (state reference standard), IRS (in-house reference standard), as well as standards specially created for interlaboratory comparisons that should be stable and homogeneous.

Pursuant to the “Policy of the Federal Accreditation Service for proficiency testing through interlaboratory comparison (comparative) tests” [2], the participation of accredited laboratories in ICT is mandatory. A laboratory should take part in ICT programs at least once a year. Within five years from the moment of making a decision on accreditation, an accredited laboratory should take part in ICT on all test methods included in the field of accreditation.

To date, the Federal Accreditation Service and the National Accreditation Institute have created a platform for laboratory proficiency testing programs, which allows the laboratory (organization) to indicate the necessary information about comparisons (samples) and obtain data on accredited providers who are ready to conduct the ICT of interest.

Both providers and laboratories are interested in constant updating of information on this platform. At the moment, there are several areas in testing, the demand for which is increasing among laboratories, and there are no providers ready to organize such comparisons. This is due to the specifics of the activities of laboratories (radiation, nuclear, medical, food), and as a consequence, with the difficulty of manufacturing (acquiring) a sample for control (SC) or with the impossibility of ensuring its homogeneity and stability.

Participation in interlaboratory comparison tests is a serious and important procedure, according to the results of which a conclusion is issued on the quality of the tests (measurements) performed. No one is immune to errors, and a participant can sometimes receive an unsatisfactory result of external control. Only by conducting competent corrections of mistakes, identifying the reasons for the unsatisfactory result, one can understand what needs to be done to improve the quality of services, thereby meeting the high-level requirements of both Russian and international standards.

In order to remain competitive and conduct successful economic activities, it is necessary to regularly confirm the quality of the services provided. From a practical point of view, participation in interlaboratory comparison tests is a universal way to demonstrate the technical competence of an organization. Organizations that regularly participate in interlaboratory comparisons and show high quality of work performance cause trust in the consumer, who, as it is known, always chooses trusted, reliable and high quality service providers.

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METROLOGICAL ASSURANCE OF PHTHALATES CONTENT MEASUREMENTS. CERTIFIED REFERENCE MATERIAL OF SIX PRIORITY PHTHALATES IN METHANOL

Alexandra G. Budko, Alena Y. Mikheeva, Irina Y. Tkachenko, Anatoliy I. Krylov

D.I. Mendeleyev Institute for Metrology (VNIIM), Saint Petersburg, Russia
ORCID 0000-0002-4288-2916, e-mail: a.g.budko@vniim.ru

Keywords: certified reference materials, phthalates, certified value, uncertainty, metrological traceability, mass balance method, homogeneity, stability, metrological assurance

Currently there are wide ranges of certified reference materials (hereinafter referred to as RM) in Russian Federation. The RM constitute an important part of ensuring the uniformity of measurements. Nevertheless, at the present moment there are groups of organic compounds without correspondent RMs, e.g. ortho-phthalic acid ester (phthalates).

Phthalates belong to bulk products in chemical industry. They were most commonly used as PVC products plasticizer in different polymer materials for industrial, domestic, food and medical applications.

In phthalate group, there are six compounds to be classified as priority organic pollutants.

Measurement methods for phthalates content in different types of matrixes are secured in reference documents of Russian Federation and Technical Regulations of the Customs Union.

As it was indicated above, certified RMs (CRM) for phthalates in Russian Federation have not been developed. Currently, the CRM produced by National institute for metrology of China (NIM), National Metrology Institute of Japan (NMIJ), National Institute of Standards, and Technology, USA (NIST) are available in order to measure phthalates provided with metrological traceability.

According to international approaches [1], the traceability assurance basis in organic analysis is fully defined pure organic matter (CRM). Consequently, the first necessary step to produce CRM and to form the chain of traceability is a detailed analysis of pure organic substance for further certification.

All the measurements were made using State primary standard of mass (molar) units and mass (molar) concentration of organic compounds in liquid and solid substances based on liquid and gas chromatography-mass spectrometry with isotope dilution and gravimetry – GET 208.

Prior to purity determination of the individual phthalates, identification of the purchased pure organic substances was conducted. The determination of the initial substance was made with mass balance method, which suppose pure organic substance measurement for 4 possible groups of impurities (related compounds - RC, water, volatile organic compounds (VOC) and nonvolatile compounds (NC)) with subsequent mass fraction calculation for the main component according to the formula: "100% minus sum of impurities" [2]. As phthalates can be classified as organic substances suitable for purification by distillation (sublimation) at atmospheric and/or reduced pressure, the determination of impurities RC and VOC was carried out simultaneously within one measurement.

In all investigated pure organic substance, typical impurities were registered. The presence of these impurities is determined by the production technology (alcohols, benzoic acid esters, phthalic anhydride, and isomeric phthalates).

The mass fraction of VOCs and RCs in pure substances ranged from 0.17 % to 1.12 %.

The mass fraction of non-volatile compounds was less than 0.0005 %.

The mass fraction of water was in the range from 0.027 % to 0.105 %.

The CRM was prepared in the research department of state standards of organic and inorganic analysis of VNIIM by weight and volume-weight methods.

The mass concentration and mass fraction value of individual phthalates in the prepared solution was evaluated via the calculation and experimental preparation procedure.

The sample obtained was tested for homogeneity and stability in accordance with GOST (National State Standard) ISO Guide 35—2015 [3]. The CRM metrological characteristics for the solution composition of esters of ortho-phthalic acid (phthalates) in methanol are presented in Table 1.

Table 1 The CRM metrological characteristics for composition of phthalates solution in methanol

Name of compound	**Range of acceptable certified values of the component's mass concentration of the, mg/mL**	**Range of acceptable certified values of the component's mass fraction, mg/g**	**The relative expanded uncertainty *U (k*=2)*, %**
Dimethyl phthalate	1,90 ÷ 2,10	2,40-2,65	2
Diethyl phthalate	1,90 ÷ 2,10	2,40-2,65	
Di(n-butyl) phthalate	1,90 ÷ 2,10	2,40-2,65	
Benzyl butyl phthalate	1,90 ÷ 2,10	2,40-2,65	
Di(2-ethylhexyl) phthalate	1,90 ÷ 2,10	2,40-2,65	
Di(n-octyl) phthalate	1,90 ÷ 2,10	2,40-2,65	
* Corresponds to the limits of the allowed relative total error (±δ, %), P=0,95.			

The CRM is registered with the Federal Information Fund for Ensuring the Uniformity of Measurements, registration number GSO 11366-2019.

The CRM of phthalates in methanol was used as a measuring instrument for calibration of analytical equipment for development of a reference method for measuring the mass fraction of six priority phthalates in objects based on polyvinyl chloride by gas chromatography / mass spectrometry with isotope dilution, VNIIM-243-02 -2019 [4].

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METROLOGY FOR STABLE ISOTOPE MEASUREMENTS

Ian K. Chubchenko[1,2], Anna V. Kolobova[1]

[1] D.I. Mendeleyev Institute for Metrology (VNIIM), Saint Petersburg, Russia
[2] ITMO University, Saint Petersburg, Russia
ORCID: 0000-0002-3408-5116, e-mail: ycc@b10.vniim.ru

Keywords: metrology, stable isotopes, isotope ratio mass spectrometry, isotope ratio infrared spectroscopy, certified reference materials, urea breath test, international key comparison, interlaboratory comparison

The relevance of using isotope analysis in various fields of human scientific and technical activity has been shown in a large number of scientific papers, for example [1-3]. We will mention only a few of the most important applications from the field of medicine, food industry and ecology:

- urea breath test can diagnose the presence of the bacterium Helicobacter Pylori in the human stomach, which causes stomach cancer [4],
- isotope analysis is widely used for food quality control [5],
- analysis of isotopes in atmospheric air allows us to assess the impact of anthropogenic processes on the content of greenhouse gases in the atmosphere [6].

For all the tasks presented above, there are a number of significant issues in terms of ensuring the uniformity of measurements, and, consequently, the reliability of the results obtained.

In accordance with the resolution of the International Bureau of Weights and Measures (hereinafter – BIPM) [7], measurements of delta values of isotope ratios are currently traceble not to the International system of SI units, but to international reference materials (hereinafter - RM), which form the international delta scale of stable isotopes. The instability of some RM detected in recent years [8] has led to problems in the field of metrological support for measurements of stable isotopes.

In order to ensure the uniformity of measurements and exchange of information at the international level, an isotope ratio working group was formed in 2017 within CCQM. Representatives of the D.I.Mendeleyev Institute for Metrology are part of this group and regularly participate in meetings.

International comparisons were organized within the framework of the isotope ratios working group: CCQM-K167 «Carbon isotope delta measurements of vanillin», CCQM-P212 «Coherence of carbon isotope delta reference materials», CCQM-P204 «CO_2 isotope ratios (δ^{13}C и δ^{18}O) in pure CO_2», CCQM-P213 «Delta copper isotope ratio measurements in high purity materials».

A measurement standard (hereinafter referred to as MS1) for carbon isotope ratio measurements in gas mixtures of carbon dioxide [9], which is part of the Russian primary measurement standard GET 154-2019, had been developed. It has been used to participate in all comparisons with the exception of CCQM-P204. Projects of mutually beneficial cooperation with BIPM and the national metrological Institute of Germany PTB allowed to modernize EU1 and achieve higher repeatability and reproducibility of measurements, as well as to publish a number of joint scientific papers [10-12].

In order to develop international cooperation in the field of stable isotope ratio metrology, we are going to participate in the 19env05 STELLAR European project "Stable isotope metrology to enable climate action and regulation ", organized by the regional metrological organization EURAMET.

International cooperation makes it possible to develop a common approach for ensuring the uniformity of measurements in the framework of isotope analysis and to suggest optimal ways to build a system of metrological support for measurements of stable isotopes at the national level.

At the moment, there are a number of unresolved issues at this level. The Federal information fund for ensuring the uniformity of measurements has registered isotope mass spectrometers under №№ 25833-03, 60027-15, 43245-09, 27959-04, which are also used in the diagnosis of diseases caused by Helicobacter Pylori infection. However, metrological traceability to the international delta scale is not provided, and the main normalized metrological characteristic is the standard deviation of output signal.

When performing sample analyses in accordance with [13-16], the traceability of measurement results to the international delta scale is ensured by using international reference materials.

The lack of local isotope ratio reference materials, together with the sanctions policy of a number of countries, leads to a deterioration in the accuracy of measurements performed by Russian laboratories. The latest inter-comparison test organized by D.I.Mendeleyev Institute for Metrology UV 242/39.20 "Delta values of carbon isotope ratios ($\delta^{13}C$) in vanillin" showed significant discrepancies up to 0.8% among the twelve participants, while the standard deviation of individual results in most cases did not exceed 0.07%.

In Russia, the isotope breath test is available in most well-known medical laboratories and clinics, more than 10,000 tests are performed monthly, and more than 40 devices are used to perform it. However, these devices are not listed in the registry. This means that they do not pass state tests and subsequent verification, and traceability to the international delta scale is not provided. For metrological support of diagnostics of diseases caused by Helicobacter Pylori infection, a measurement standard based on an isotope mass spectrometer (hereinafter referred to as MS2) is being developed within the framework of the national project System–2020-M. EU2 will allow the development of carbon dioxide reference material with a known isotopic composition, necessary for verification, calibration and testing in order to approve the type of isotope analyzers used for the isotope breath test. The creation of EU2 and subsequent development of reference material will increase the reliability of performed isotope urea breath tests. In addition, EU2 will allow further development of methods for measuring the isotopic composition of C, O, N, and H of other specific gases-markers of exhaled air to study the dynamics of physiological processes for the purpose of early detection of diseases and monitoring the effectiveness of therapy. Improvement of EU2 in the future will allow to develop reference materials of C, O, N, H isotopes in atmospheric air to solve the tasks of the national project "Ecology", as well as isotopic reference materials to ensure food quality control.

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DEVELOPMENT OF THE APPROVED TYPE REFERENCE MATERIAL OF PLUTONIUM DIOXIDE MASS FRACTION AND ISOTOPIC COMPOSITION AND ITS APPLICATION

E.V. Chukhlantseva, Yu.A. Tadevosyan, O.V. Starovoytova, O.V. Stepanova,
M.A. Semyonov, V.V. Plekhanov, I.M. Maksimova

Mayak Production Association, Ozyorsk, Russia
e-mail: cpl@po-mayak.ru

A. A. Bochvar High-Technology Scientific Research Institute for Inorganic Materials, Moscow, Russia
e-mail: post@bochwar.ru

Keywords: development and application of the reference material, accounting for nuclear materials, plutonium dioxide, coulometry, spectrophotometry, isotopic composition, plutonium mass fraction

FSUE Mayak PA (Ozyorsk, Chelyabinsk Region) developed the approved type reference material (hereinafter referred to as RM) of plutonium dioxide mass fraction and isotopic composition [1, 2].

Experimental works on determination of the certified value of the mass fraction of total plutonium were performed with the help of the PIK-100 M coulometric potentiostate – integrator designed by the FSUE Ural Research Institute for Metrology using the industry-specific technique [3] certified by the A.A. Bochvar High-Technology Scientific Research Institute for Inorganic Materials. Experimental works on determination of the isotopic composition were carried out by the TRITON Plus solid-phase mass-spectrometric unit using the industry-specific technique [4].

The reference material that is manufactured according to the enterprise process regulations consists of plutonium dioxide powder fabricated at the Mayak PA. The container was sampled in the middle of a long-term campaign of spent fuel reprocessing characterized by a constant burn-up range in the absence of impact of fluctuations of individual process parameters. Homogeneity of plutonium dioxide powder in terms of the basic substance mass fraction is ensured by the material fabrication method.

Determination of values of the RM metrological characteristics was performed according to the algorithm of RM certification specified in the state standard [5]. Table 1 presents metrological characteristics of the RM.

Table 1. Metrological characteristics of the reference material of plutonium dioxide mass fraction and isotopic composition in plutonium dioxide

Characteristic to be certified	**Units**	**RM value certified as of 01.05.2018**	**Range of absolute error of the certified value of RM at P = 0.95**	**Adjusted certified values of RM as of 01.11.2020**
Mass fraction of Pu	%	87.40	0.13	86.59
Mass fraction of Pu^{238} isotope	%	2.491	0.008	2.465
Mass fraction of Pu^{239} isotope	%	63.515	0.016	64.105
Mass fraction of Pu^{240} isotope	%	21.016	0.011	21.207
Mass fraction of Pu^{241} isotope	%	7.548	0.008	6.746
Mass fraction of Pu^{242} isotope	%	5.426	0.013	5.477

The reference material is packed by (1.0 ± 0.10) g of plutonium dioxide into glass bottles (with a capacity of not more than 2 cm^3) with screw caps equipped with radiation resistant gaskets.

At the Mayak PA the reference material is used:

1. In the system of accounting for and control of nuclear materials;
2. For quality control of measurements of:

- Pu mass fraction in plutonium products using mass-spectrometric, coulometric, spectrophotometric, γ-spectrometric and isotope dilution α-spectrometric methods;
- isotopic composition of plutonium and plutonium products using γ- and α-spectrometric methods;

3. For calibration, graduation and verification of instrumentation;
4. For transfer of the size of unit to the reference materials of lower categories.

Currently, the reference material of plutonium dioxide mass fraction and isotopic composition is used in the implementation of the technique for measuring plutonium mass fraction in plutonium dioxide at the new UPK-19 potentiostate coulometric unit installed in the analytical laboratory of the Siberian Chemical Combine.

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ABOUT NEW REFERENCE MATERIALS DENSITY AND VISCOSITY

Alexey A. Demyanov, Anastasiya A. Neklyudova

D.I. Mendeleyev Institute for Metrology (VNIIM), Saint Petersburg, Russia
Researcher ID O-3983-2018, A.A.Demyanov@vniim.ru
Researcher ID O-3887-2018, A.A.Tsurko@vniim.ru

Keywords: reference materials, dynamic viscosity, kinematic viscosity, density, working standards

The work is devoted to the development and study of reference materials of dynamic, kinematic viscosity and density of a liquid based on pure mineral and synthetic oils. The relevance of the work is due to the need to create new means of verification for measuring instruments of viscosity and density, used in the field of state regulation of ensuring the uniformity of measurements in the Russian Federation.

In order to create a basis for the development and research of new reference materials of viscosity, the working standard of the unit of kinematic viscosity of the first discharge fluid and the working standard of units of the dynamic and kinematic viscosity of the fluid of the second category were improved in accordance with the updated document «State system for ensuring uniformity of measurements. State verification scheme for measuring instruments for viscosity of liquids», approved by order of the Federal Agency on Technical Regulating and Metrology (Rosstandart) 05.11.2019, № 2622 [1].

The studies carried out made it possible to develop six new types of reference materials for fluid viscosity, certified in the temperature range from minus 40 °C to 150 °C, the certified values of which were established with a relative expanded uncertainty from 0.2 % to 0.4 % with a coverage factor k=2 , as well as three types of new reference materials for liquid density, the certified values of which were established with an expanded uncertainty of 0.02 kg/m^3 at a coverage factor of k=2.

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ON THE DEVELOPMENT OF METROLOGICAL SUPPORT FOR SAFETY CONTROL OF COAL COMBUSTION WASTE

Svetlana A. Epshtein[1], Olga S. Golynets[2], Tatyana O. Guschchina[1], Maria Yu. Medvedevskikh[2]
[1] NUST "MISiS", Moscow, Russia
Researcher ID: B-2080-2016, ORCID.0000-0001-8356-4319, e-mail: apshtein@yandex.ru
[2] UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
Researcher ID: G-6171-2017, e-mail: lab241@uniim.ru

Keywords: reference materials, safety indicators, fluorine, coal, ash and slag wastes

Modern energy, increasing the volume of solid fuel processing, is also increasing the amount of waste, which today is about 40% of the total amount of industrial waste and is estimated at about 90 million tons per year. At the same time, the volume of ash and slag waste accumulated in Russia is approaching 2 billion tons, located on territories of more than 22,000 hectares.

Waste from the production of some deposits is fully used by the enterprises for filling the mined-out space of the open-pit mines and reclamation. Ash and slag waste from heat and power plants, hydropower plants, boiler houses and air heating plants are stored in ash dumps, however, they are currently considering the use of them as components of mixtures for sealing degassing wells, filling material in mined-out areas of mines and recultivators for restoring disturbed lands of coal mines. For the further use of solid waste, it is necessary to study and establish the differences in the content of mobile forms of macro- and microelements in the wastes of mining and processing of coals from different basins, deposits and their separate areas for the subsequent assessment of the emission of potentially hazardous elements into the environment when using waste.

The draft technical regulation of the Customs Union "Requirements for coals and products of their processing" as one of the main goals provides for the protection of human life and health, property, the environment and contains safety requirements and compliance with these requirements. However, in the list of products for which the requirements of the technical regulations of the Customs Union are established, there are no products of thermal processing of coal. In recent publications, it has been shown that the content of water-soluble forms of macro- and microelements is significant, and the degree of transition to the aquatic environment of such elements as fluorine, sulfur, arsenic, manganese, strontium and iron for various wastes of coal combustion (ash and slag waste, fly ash and slag, obtained by burning coal at heat and power plants, hydroelectric power plants or boiler houses) is significant [1]. At the same time, there is no methodological base that would allow assessing the impact of waste on the environment during storage and recycling.

Currently, the development of methods has begun to determine the mobile forms of macro - and microelements from the waste of coal mining and combustion to assess the emission of potentially hazardous elements into the environment when using waste to restore disturbed lands, reclamation and use in mined areas of mines and open pits.

The variety of components to be determined in coal processing products entails an increase in the number of measurement procedures (methods) used. Current and newly emerging instruments for measuring the composition of coals and products of their processing are based on various physicochemical analytical methods. The analysis of the available reference materials of the approved type for metrological support of such instruments showed an insufficient number of them to control the accuracy of measurement methods used in determining the composition of ash and slag waste, fly ash, coal slags, as well as for calibration, verification and testing of measurement instruments in type approval purposes and the complete absence of reference materials (CRMs) of coals and products of their processing with a certified fluorine value. Therefore, the development of new types of CRMs that meet the modern requirements established in [2] is required.

In 2019, specialists of the UNIIM-Affiliated branch of the D.I. Mendeleyev Institute for Metrology, together with the Federal State Autonomous Educational Institution of Higher Education "National Research Technological University" MISiS (NUST "MISiS") have developed and approved a CRM of the mass fraction of total fluorine in the coal of the Kuznetsk Basin (CH-1 CRM MISiS) in the framework of activities on metrological support of measurement instruments of the coal industry. Metrological characteristics of CRM for the composition of coal are presented in Table 1.

Table 1. Metrological characteristics of CRM for the composition of the mass fraction of total fluorine in the coal of the Kuznetsk Basin (CH-1 CRM MISiS)

Certified characteristic	**Range of certified CRM values, µg/g (ppm)**	**Limits of permissible values of the absolute error of the CRM value (P = 0.95), µg/g (ppm)**
Mass fraction of total fluorine	25 – 200	± 6
Note: The certified characteristic is based on the material dried at 105 ºC		

This CRM was developed using matrices of Russian coal deposits.

Conclusions

1. The analysis showed the problem of the lack of a methodological base, which would allow assessing the impact of waste on the environment.

2. The analysis showed the problem of a lack of CRM required for metrological support of coal industry enterprises in terms of monitoring the safety of wastes from lignites and hard coals combustion.

3. According to the results of successful tests, a reference material of the mass fraction of total fluorine in the coal of the Kuznetsk Basin (CH-1 CRM MISiS) GSO 11484-2020 was entered into the State Register of Approved Types of CRMs of the Russian Federation, the material of which is matrices of coals of Russian deposits.

4. The work of UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology, together with NUST "MISiS", continues on the development and approval of a series of CRMs of coal composition with certified safety characteristics based on solid fuel from Russian deposits.

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DEVELOPMENT OF A MULTI-COMPONENT STANDARD SAMPLE FOR VERIFICATION AND CALIBRATION OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETERS

Ianina I. Ermakova, Alexander V. Ivanov, Irina N. Zyablikova, Anna N. Shobina

The All-Russian Research Institute for Optical and Physical Measurements, Moscow, Russia
e-mail: vniiofi@vniiofi.ru

Keywords: standard sample, metal ions, multi-component standard sample, calibration

There has been a significant increase in the technical level of industry in various fields in the modern world. New advanced materials and substances with more complex compositions are constantly appearing. This is followed by increased requirements for the accuracy of quality control of these objects. As a result, the range of analytical equipment that implements physical and physico-chemical methods of analysis is expanding. But until now, most of the methods remain relative, that is, requiring calibration. In accordance with modern requirements, in order to implement these methods of quality control, almost any object uses reference materials.

In addition to accuracy, the method must be fast, sensitive, and accessible. This is why inductively coupled plasma mass spectrometry is becoming increasingly popular. Mass spectrometers are available on the market in a wide range of prices, configurations, and capabilities.

Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry characterized by high sensitivity and the ability to detect both metal and non-metal ions in concentrations up to 10^{-10} %. The method is based on the use of inductively coupled plasma as a source of ions and a mass spectrometer for their separation and detection. ICP-MS also allows isotopic analysis of the selected ion.

However, the main serious disadvantage of the method is the mandatory configuration of these types of devices using the manufacturer's multi-component solution.

The cost of this solution is small, but due to delivery from abroad and the high dollar exchange rate in Russia, the cost per bottle becomes unavailable for many businesses.

Table 1 shows an example of the composition of a multicomponent solution for setting up and calibrating a mass spectrometer with an inductively coupled plasma of imported production.

VNIIOFI has started developing a multi-component solution for verification and calibration of inductively coupled plasma mass spectrometers. According to its metrological characteristics, it will be no worse than imported analogues, but much more affordable. Also, the developed sample will be certified in the CRM rank, which will allow using this solution as a means of checking devices that are in the sphere of state regulation. The planned composition of the multicomponent solution produced by FSUE VNIIOFI is shown in table 2.

Table 1. The omposition of multi component solution Agilent 7500 Series PA Tuning 1

Element	C, µg/ml	Source material	Purity of the source material	Element	C, µg/ml	Source material	Purity of the source material
As	20,0	As	99,99+	In	5,00	In	99,99+
Be	20,0	$Be_4O(CH_3COO)_6$	99,99+	Li^6	5,00	$^6Li_2CO_3$	99,99+
Cd	20,0	Cd	99,99+	Lu	5,00	Lu_2O_3	99,99+
Zn	20,0	Zn	99,99+	Mn	5,00	Mn	99,99+
Mg	10,0	Mg	99,99+	Na	5,00	$NaHCO_3$	99,99+
Ni	10,0	Ni	99,99+	Sc	5,00	Sc_2O_3	99,99+
Pb	10,0	PbO	99,99+	Sr	5,00	$Sr(NO_3)_2$	99,99+

Element	C, µg/ml	Source material	Purity of the source material	Element	C, µg/ml	Source material	Purity of the source material
Al	5,00	Al	99,99+	Th	5,00	$Th(NO_3)_4 \cdot 4H_2O$	99,99+
Ba	5,00	$Ba(NO_3)_2$	99,99+	Tl	5,00	$TlNO_3$	99,99+
Bi	5,00	Bi	99,99+	U	5,00	$UO_2(NO_3)_2 \cdot 6H_2O$	99,99+
Co	5,00	Co	99,99+	V	5,00	NH_4VO_3	99,99+
Cr	5,00	$Cr(NO_3)_3 \cdot 9H_2O$	99,99+	Y	2,50	$Y(No_3)_3 \cdot 6H_20$	99,99+
Cu	5,00	Cu	99,99+	Yb	2,50	Yb_2O_3	99,99+

Table 2 Planned composition of multicomponent solution the production of the FSUE "VNIIOFI»

Element	C, µg/ml	Source material	Purity of the source material	Element	C, µg/ml	Source material	Purity of the source material
Be	20,0	$Be_4O(CH_3COO)_6$	99,99+	Cu	5,00	Cu	99,99+
Cd	20,0	Cd	99,99+	In	5,00	In	99,99+
Zn	20,0	Zn	99,99+	Li^6	5,00	$^6Li_2CO_3$	99,99+
Mg	10,0	Mg	99,99+	Mn	5,00	Mn	99,99+
Ni	10,0	Ni	99,99+	Na	5,00	$NaHCO_3$	99,99+
Pb	10,0	PbO	99,99+	Sc	5,00	Sc_2O_3	99,99+
Al	5,00	Al	99,99+	Sr	5,00	$Sr(NO_3)_2$	99,99+
Ba	5,00	$Ba(NO_3)_2$	99,99+	Tl	5,00	$TlNO_3$	99,99+
Bi	5,00	Bi	99,99+	V	5,00	NH_4VO_3	99,99+
Co	5,00	Co	99,99+	Y	2,50	$Y(No_3)_3 \cdot 6H_20$	99,99+
Cr	5,00	$Cr(NO_3)_3 \cdot 9H_2O$	99,99+				

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REQUIREMENTS FOR REFERENCE MATERIAL USED IN THE LABORATORY IN ACCORDANCE WITH FEDERAL LAW No. 102 OF 26.06.2008, GOST ISO/IEC 17025-2019, TEST METHODS AND ACCREDITATION CRITERIA. RISKS FOR LABORATORIES DUE TO DIFFERENCES IN REQUIREMENTS

Dmitrii V. Falkin

Accraditation Centre “Standart”, Samara, Russia
e-mail: adar-rf@mail.ru

Keywords: laboratory accreditation, general requirements for laboratory competence, use of reference materials and reagents, traceability, metrology, risk assessment

The use of reference material in laboratory practice is quite diverse: 1) for verification and calibration of measuring instruments, i.e. 2) for SI calibration 3) for in-laboratory quality control of measurements 4) for input control of reagents.

If the activity for which the laboratory performs measurements is within the scope of state control in the field of ensuring the uniformity of measurements, then for 1) and 2) - reference materials reference materials must be of an approved type, i.e. have the status of RM, in accordance with [1] Article 8. CH 2. in the sphere of state regulation of ensuring the uniformity of measurements, reference materials of approved types are used.

For 3), 4) the requirements for reference materials are formulated by the laboratory independently. However, if the laboratory is accredited to meet the requirements of [2], the laboratories must establish and maintain metrological traceability. If direct measurements are implemented in the laboratory, then everything is clear: the SI must be verified (calibrated) by an organization that meets [2] and verification documents must contain information about the standards used during verification. If calibration is required to obtain the measurement result, then reference material must be used and in accordance with the requirements of paragraph 6.5.2 of [2], the Laboratory must ensure traceability of the measurement results to the International system of units (SI) by: b) certified values of certified reference materials from a competent manufacturer with the specified metrological traceability to SI (note 2-reference materials Manufacturers that meet the requirements of ISO 17034 are considered competent). But there are very few such accredited manufacturers. This means that in accordance with the requirements of Annex a of [2], it is necessary to have information about which reference point the sample used by the laboratory is traced to. This information is not available in the fgis ARSHIN, and in most cases this information is not available in the CRM Passports. And laboratories need to contact the manufacturer for more information. If the information is provided, the requirement is met, and if not, you need to look for a new supplier. There are also situations when traceability data is available only for samples that are not in the CRM status, such as CO, SOP, etc. In this case, the requirements of [2] are met, but they are not met with the requirements of [1]. Also, in this case, a discrepancy with one of the points may be recorded [3]. Moreover, not confirmed the metrological traceability is one of the grounds for suspension of accreditation in accordance with [4].

Total laboratory shall have reference material for compliance with [1] they should be in the status of the bonds, and to comply with [2] and [3] they must contain traceability information. Otherwise, adverse events may occur: penalties for failure to comply with legislation in the field of ensuring the uniformity of measurements, suspension or refusal of accreditation, failure to fulfill obligations to the customer, penalties under the administrative Code.

In summary, we consider it necessary to recommend that laboratories carefully study information about the traceability of reference material, as well as the status of reference material.

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DEVELOPMENT OF STANDARD REFERENCE MATERIALS FOR METROLOGICAL ASSURANCE OF WATER'S COLORITY MEASUREMENTS

Lyudmila I. Goryaeva, Eugenia P. Shchukina

UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
e-mail: ShchukinaEP@uniim.ru

Keywords: water's colority, chrome-cobalt colority scale, measurement procedure, standard reference material, metrological traceability

Colority is a conventionally accepted quantitative characteristic for describing the color of natural waters, drinking water, and water solutions that have a slight color. The color of natural waters and drinking water is usually due to the presence of colored substances in them – iron and other metals, humic and fulvic acids associated with soil humus, as well as various man-made pollutants. Measuring the colority of natural waters is necessary for the correct choice of drinking water treatment technology.

The color of water is determined by visual or photometric methods by comparison with solutions of a specially prepared color scale and expressed in degrees of color of this scale. Currently, both in Russia and abroad, two empirical color scales of water and aqueous solutions are used: platinum-cobalt (Hansen scale) and chromium-cobalt [1-5]. The chromium-cobalt scale was developed as a more affordable analog of the platinum-cobalt color scale, the preparation of which involves the use of expensive potassium hexachloroplatinate. Both the platinum-cobalt and the chromium-cobalt color scales are obtained by diluting the corresponding basic standard solution, which is conditionally assigned a certain color and which is prepared according to the established recipe.

Most of the standardized methods used in Russia for measuring the colority of natural, drinking and waste water and water solutions are based on using of the chromium-cobalt scale [1-3]. The metrological characteristics of the most common chromaticity measurement methods in Russia are shown in table 1.

Table 1. Metrological characteristics of methods for measuring the chromaticity of drinking, natural surface and treated wastewater on the chromium-cobalt scale by photometric method

Document on the measurement procedure	**Range colority measurements, degrees of color (Cr-Co)**	**Repeatability limit, r**	**Reproducibility limit, R**	**Error bounds of measurement result at P=0,95**
RD 52.24.497-2019	5 – 20	1+0,006X	1+0,01X	2
	20 – 500	1+0,006X	1+0,01X	± (3+0,03X)
PND F 14.1:2:4307-04	1 – 10	15 %	20 %	± 40 %
	10 – 50	7,5 %	10 %	± 20 %
	50 – 500	3 %	5 %	± 10 %
GOST 31868-2012	1 – 10	28 %	40 %	± 30 %
	10 – 50	17 %	24 %	± 20 %

X – measurement result.

Since colority is an empirical value, it is only possible to compare the results of colority measurements obtained in different laboratories if these laboratories use the same measurement procedure, in particular, when measurements are performed at the same wavelength.

The accuracy of color measurements of water samples depends on a number of factors: the accuracy of the wavelength setting, the purity of the cuvette, the sample temperature, and, above all, the quality of the main standard solution.

In 2019, the Scientific-research Institute of Metrology UNIIM developed a set of two standard reference materials for metrological assurance of water colority measurements on the chromium-cobalt scale.

The standard reference material of water colority on the chromium-cobalt scale (SRM Cr-Co) is intended for the preparation of the chromium-cobalt scale that is then used for calibration and verification of colority measuring instruments. The material of SRM Cr-Co is an aqueous solution of potassium dichromate and cobalt sulfate with the addition of sulfuric acid. For the preparation of SRM material, 7-water cobalt sulphate and potassium dichromate with a mass fraction of the main substance at least 99.5%, water of the first degree of purification and sulfuric acid are used. The mass fractions of the main substance in potassium dichromate and cobalt sulphate are determined by certified titrimetric measurement procedures using standard reference materials traceable to the state primary standard.

The SRM Cr-Co is packaged at least 10 cm^3 in dark glass ampoules. The shelf life of SRM is 2 years.

Metrological characteristics of SRM Cr-Co are shown in table 2.

Table 2. Metrological characteristics of SRM Cr-Co

Certified characteristic of SRM	**Certified value**	**Relative extended uncertainty for k=2, %**
Colority, degrees of Cr-Co scale	500	2,0

The standard reference materials of natural water mineral composition imitates colored natural water (SRM MSV Tsv). The main purpose of this SRM is to control the measurements accuracy of the colority on the chromium-cobalt scale as well as the mass concentration of nitrate ions, chloride ions, fluoride ions, phosphate ions, sulfate ions, total iron, chromium and cobalt in drinking, natural surface and treated wastewater. SRM can also be used for certification of methods for measuring the composition and colority of water. The SRM material is a homogeneous mechanical mixture of inorganic substances with a particle size of no more than 0.05 mm. For the preparation of SRM material commercially available reagents were used. When choosing reagents, we took into account their hygroscopicity, solubility in water, melting point, lack of interaction between substances after mixing in dry form and after dissolution in water, stability the composition of SRM material when heated to remove adsorbed water, the maximum permissible concentrations in drinking water and natural water for ions arising from dissociation of each source substance in water, and the colority of solution. In each of the reagents used for the preparation of SRM material the mass fraction of the main substance is measured according to certified titrimetric measurement procedures using standard reference materials traceable to the state primary standard. Iron is an indicator of the homogeneity of the SRM material. The standard uncertainty from possible inhomogeneity of the SRM material does not exceed 1 %. The material of SRM MSV Tsv is packed in (250 ± 3) mg, is placed in a bag made of tracing paper and sealed in a plastic film along with the label. The shelf life of SRM is 3 years. Metrological characteristics values of SRM MSV Tsv are shown in table 3.

Table 3. Metrological characteristics of SRM MSV Tsv

Certified characteristic	**Certified value**	**Relative extended uncertainty for k=2, %**
Mass concentration of nitrate ions (NO_3^-), mg/dm^3	1 – 75	3,5
Mass concentration of chloride ions (Cl^-), mg/dm^3	5 – 75	3,5
Mass concentration of fluoride ions (F^-), mg/dm^3	0,1 – 1,5	3,5

Certified characteristic	**Certified value**	**Relative extended uncertainty for k=2, %**
Mass concentration of phosphate ions (PO_4^{3-}), mg/dm^3	0,2 – 10	3,5
Mass concentration of sulfate ions (SO_4^{2-}), mg/dm^3	5 – 200	3,5
Mass concentration of total iron, mg/dm^3	0,05 – 0,50	3,5
Mass concentration of chromium хрома, mg/dm^3	0,05 – 0,7	3,5
Mass concentration of cobalt, mg/dm^3	0,5 – 8,5	3,5
Colority, degrees of Cr-Co scale	1 – 10	7

The certified values of SRM Cr-Co and SRM MSV Tsv are set according to preparation procedure in accordance with RMG 93-2015 [6].

The certified values of these SRMs are traced to the certified values of standard reference materials of potassium dichromate, sodium chloride, Trilon B with established traceability to State primary standard of units of mass (molar) fraction and mass (molar) concentration of the components in liquid and solid substances and materials based on coulometry.

SRM Cr-Co and SRM MSV Tsv are included in the State register of approved types of standard reference materials under the numbers GSO 11398-2019 and GSO 11432-2019, respectively.

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ENSURING THE UNIFORMITY OF MEASUREMENTS IN THE FIELD OF LABORATORY MEDICINE. DEVELOPMENT OF A STANDARD GLUCOSE SAMPLE IN BLOOD SERUM

Natalia Yu. Griazskikh, I.N. Zyablikova, Alexander V. Ivanov, Anna N. Shobina

The All-Russian Research Institute for Optical and Physical Measurements (VNIIOFI),Moscow, Russia
e-mail: vniiofi@vniiofi.ru

Keywords: state standard sample, glucose, blood serum

Measurement of serum glucose is one of the most important factors in the diagnosis of diabetes. Currently, blood glucose is measured using several methods. When self-monitoring at home, systems for self-diagnosis of blood glucose (glucose meters) are used, the principle of operation of which is based on measuring glucose by an enzymatic method using test strips (glucose oxidase, glucose dihydrogenase methods). However, the accuracy of these methods is 15-20 %. Requirements for blood glucose monitoring systems for self-monitoring in the treatment of diabetes are described in GOST R ISO 15197-2015 " Test systems for in vitro diagnostics. Requirements for blood glucose monitoring systems for self-monitoring in the treatment of diabetes and prescribing treatment".

According to GOST ISO 17511-2011 " medical Devices for in vitro diagnostics. Measurement of values in biological samples. Metrological traceability of values attributed to calibrators and control materials " the ideal end point of the traceability chain is to determine the appropriate unit of the International system of units (SI), but the choice of stages and levels at which traceability ends for this value depends on the availability of measurement techniques and higher-level standards. In many cases, the traceability of measurements cannot currently be carried out to a higher order level than the method chosen by the manufacturer or the manufacturer's working calibrator. In such cases, correctness refers to the level of the calibration hierarchy at which an internationally recognized reference measurement technique and/or standard sample (calibrator) becomes available.

According to the joint Committee on traceability in laboratory medicine (JCTLM), the main reference method for determining serum glucose is gas chromatography-mass spectrometry with isotope dilution, however, in laboratory practice, the photometric (UV-hexokinase) method is more often used.

Currently, the Russian Federation has approved standard glucose samples GSO 9279-2008, GSO 9280-2008, GSO 9281-2008 WITH the composition of GLUCOSE and LACTATE SOLUTION (Molar concentration of glucose and lactate, mmol/dm3), but these samples are not intended for use in biochemical analyzers. One of the reference methods for measuring serum glucose from JCTLM data is the hexogenase method (JCTLM CDC Hexokinase reference method for glucose human serum Spectrophotometry Neese JW et al., HEW Pub No. (CDC) 77-8330, HEW, USPHS, CDC, 1976)

FSUE "VNIIOFI" carried out work on the measurement of serum glucose in blood serum by photometric methods. The influence of temperature on reagents was studied (measurements of glucose in blood serum were performed using the RDX method at temperatures of 25 and 37 °C). Based on the obtained studies, a standard sample of glucose in blood serum was tested.

As a result of the obtained studies, the state standard sample of glucose in blood serum was tested using the photometric method of concentration measurement, which makes it possible to ensure metrological traceability of biochemical analyzers when measuring glucose in blood serum.

Currently, the Federal state unitary enterprise "VNIIOFI" is working on the approval of a standard sample of glucose in blood serum by photometric method.

All authors read and approved the final version of the manuscript

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PRODUCTION OF ETHANOL WATER SOLUTIONS REFERENCE MATERIALS IN FBI «STATE REGIONAL CENTER FOR STANDARDIZATION, METROLOGY AND TESTING IN THE NIZHNY NOVGOROD REGION»

Roman A. Ignatev, Maksim V. Zavodskoy

Federal budget institute «State regional center for standardization, metrology and testing in the Nizhny Novgorod region»
(FBI «Nizhny Novgorod CSM»), Nizhny Novgorod, Russia
e-mail: ignatev@nncsm.ru

Keywords: reference materials, certified reference materials of composition, reference materials of water solutions of ethanol, working measurement standard, comparison of measurement standards, State Primary Measurement Standard

Reference materials of the composition of ethanol water solutions are solution of ethyl alcohol in water medium with a nominal volume of 500 cm3 or 1000 cm3 in a hermetically sealed polyethylene bottle with a screw cap provided with a label and a protective sticker on the cap.

Purpose of the reference materials of the composition of ethanol water solutions:

- verification, testing, and calibration of analyzers and detectors for ethanol vapors in exhaled air, generators of gas mixtures of ethanol vapors in air, as well as control of metrological characteristics during their tests, including for type approval;
- certification of measurement procedures (methods);
- control of the accuracy of the measurement results obtained by the measurement procedures (methods) in the process of their application in accordance with the algorithms established in them.

The area of industry, production, where the reference materialscan be mainly used: health care, forensic medical examination, ensuring road safety, ensuring safe conditions and labor protection.

Currently, FBI "Nizhny Novgorod CSM" in cooperation with «D.I.Mendeleyev Institute for Metrology» creates of a working measurement standard for the unit of mass concentration of ethanol in water solutions of the 1st rank in the range of values from 0.10 to 6.0 mg / cm^3.

Purpose: Expanding the capabilities of FBI"Nizhny Novgorod CSM" in terms of the release of a new type of reference materialsof the composition of ethanol water solutions of intended for transferring a unit of mass concentration of ethanol from generators of gas mixtures of ethanol vapors in air to analyzers of ethanol vapors in exhaled air in accordance with GOST 8.578-2014 "GSE. State verification scheme for measuring instruments for the content of components in gaseous media"

The working measurement standard must ensure the transfer of a unit of mass concentration of ethanol from the State Primary Measurement Standard of units of a molar fraction, mass fraction and mass concentration of components in gas and gas condensate media GET 154-2016 to reference materials of the composition of aqueous solutions of ethanol in accordance with GOST 8.578-2014.

The metrological characteristics of the working measurement standard are determined by the requirements of GOST 8.578-2014 for generators of gas mixtures of ethanol vapors in the air, as well as the requirements for reference materialsof the composition of ethanol water solutions, which are used in combination with generators, and must ensure the release of reference materials with appropriate metrological characteristics (shown in the Table 1).

Table 1. The metrological characteristics of the working measurement standard

Defined components	**Measurement range of ethanol mass concentration, mg / cm^3**	**Extended uncertainty at k=2, %**
C_2H_5OH	from 0.10 to 6.0	1

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2. GOST 8.315-97 State system for ensuring the uniformity of measurements (GSI). Reference materialsof the composition and properties of substances and materials. Fundamentals.
3. GOST 8.563-2009 State system for ensuring the uniformity of measurements. Measurement techniques (methods).
4. Method of measuring the mass concentration of ethanol in reference materialsof the composition of aqueous ethanol solutions.

DEVELOPED NEW GENERATION OF CERTIFIED REFERENCE MATERIALS FOR METROLOGICAL SUPPORT IN THE FIELD OF SURFACE DENSITY AND COATING THICKNESS MEASUREMENTS

Vyacheslav V. Kazantsev, Alexander S. Vasilyev

UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
e-mail: kazantsev@uniim.ru

Keywords: multilayer coatings, surface density, thickness, state primary standard, certified reference materials, traceability

Our team completed the work on the R&D project Multilayer coatings in 2019. The purpose of this project was to develop CRMs for multilayer coatings, which are required for testing, verification, and calibration of X-ray fluorescence measuring instruments for thickness and surface density of coatings [1, 2].

We developed a technique for measuring surface density of two-layer metal coatings using the state primary measurement standard of surface density and mass fraction of elements in coatings GET 168-2015 [3] and algorithms for processing measurement results using the registered Program for processing measurement results for GET 168-2015 [4].

Our team completed research of CRMs homogeneity in chemical composition, which confirmed its homogeneity and the absence of impurities within the limits of detection by the X-ray fluorescence method.

We developed 12 types of CRMs for the surface density of a tin coating with a nickel sublayer on a copper base, which were approved by the Federal Information Fund for Ensuring the Uniformity of Measurements as GSO 11346-2019/GSO 11357-2019.

Table 1 shows the metrological characteristics of CRMs.

Table 1. Metrological characteristics of CRMs of two-layer coatings

Index RM	**Surface density, g/m^2**		**Thickness, µm**		**Relative measurement error, % (*P*=95%)**	
	tin	**nickel**	**tin**	**nickel**	**tin**	**nickel**
1	2	3	4	5	6	7
CO UNIIM PPT O/N/M 1	19.6	19.8	2.70	2.20	2.3	4.5
CO UNIIM PPT O/N/M 2	14.9	79.9	2.04	9.0	2.1	4.2
CO UNIIM PPT O/N/M 3	35.8	118	4.90	13.3	2.1	4.4
CO UNIIM PPT O/N/M 4	56.2	30.3	7.70	3.4	2.0	4.6
CO UNIIM PPT O/N/M 5	38.0	65.9	5.20	7.4	1.8	4.2
CO UNIIM PPT O/N/M 6	66.4	125	9.10	14.0	1.8	4.1
CO UNIIM PPT O/N/M 7	79.6	28.5	10.9	3.2	1.6	4.7
CO UNIIM PPT O/N/M 8	84.7	64.1	11.6	7.2	1.7	4.4
CO UNIIM PPT O/N/M 9	91.3	90.8	12.5	10.2	1.6	4.3
CO UNIIM PPT O/N/M 10	114.0	16.0	15.6	1.8	1.5	4.8
CO UNIIM PPT O/N/M 11	110.0	44.6	15.1	5.0	1.7	4.5
CO UNIIM PPT O/N/M 12	110.0	89.1	15.0	10.0	1.6	4.3

The developed CRMs correspond to working standards with the relative error from 2.5 to 5.0% under the state verification scheme [5].

As a result of the R&D project, developed CRMs of multilayer coatings were included in the multifunctional distributed measurement standard developed by D.I. Mendeleyev Institute for Metrology. This measurement standard was intended for use in the system of metrological support of coating thickness standards based on various operating principles, including X-ray fluorescence, eddy current and electromagnetic measurements.

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METROLOGY FOR LIFE SCIENCES AND HEALTHCARE: THE NEED AND PROGRESS IN DEVELOPING SI-TRACEABLE REFERENCE MATERIALS FOR HIGH RESOLUTION MICROSCOPY MEASUREMENTS

Ibolya E. Kepiro, Maxim G. Ryadnov

Biometrology, National Physical Laboratory (NPL), UK
ORCID: 0000-0002-8934-3389, e-mail: Ibolya.kepiro@npl.co.uk

In developing advanced medicines, a critical challenge remains to provide reproducible and quantitative measurements with traceability to the SI. High resolution microscopy, such as electron and atomic force microscopies, are routinely used these days to validate performance attributes of therapeutic and diagnostic products and technologies. However, progress towards commercialisation is hampered by the unmet need for reference calibrants that can accurately assess instrument performance and imaging results. This is of particular significance for those diagnostic measurements that rely on obtaining subcellular level details of biological specimens.

Here we present progress in the development of SI-traceable reference biomaterials, including design, characterisation, application and international inter-laboratory studies. We discuss protein paracrystalline materials, which are being used as internal calibration standards to aid differential intracellular measurements of clinical samples, and highlight the role and necessity of intercomparison studies in ensuring the repeatability and reproducibility of measurement results to support the quality, effectivity and safety of modern therapies and diagnostics.

RESULTS OF 20-YEAR PRACTICE OF HOLDING INTERLABORATORY COMPARISON TESTS OF COAL AND FUEL OIL SAMPLES

Elena N. Korchagina, Karina A. Mishina, A. A. Zarechnova

D.I. Mendeleyev Institute for Metrology (VNIIM), St.Petersburg, Russia
e-mail: E.N.Korchagina@vniim.ru

Key words: State Primary Measurement Standard, combustion calorimetry, calorific value, coal, fuel oil, interlaboratory comparison tests (ICT)

During the work under the project "System measures for the development of international cooperation and export" the Russian accreditation system was brought to the requirements of international standards in 2017. The aim of the Federal Service for Accreditation was to join the International Laboratory Accreditation Cooperation and to sign the agreement on the mutual recognition in the field of testing on calibration (ISO/IEC 17025). The status of a participant of the ILAC MRA has opened up the new opportunities for domestic exports when Russian products enter foreign markets, because the presence of the ILAC MRA mark on the product test reports is a required condition for the Russian test results to be recognized abroad.

International quality system requires testing and calibration laboratories to conduct internal audits of their activities in order to monitor the quality of performed tests and calibrations. According to GOST ISO/IEC 17025-2019 “General requirements for the competence of testing and calibration laboratories” (7.7 ensuring the quality of results), the laboratory should monitor its activities by comparing their results with other laboratories. This comparison should include the following activities or one of them:

a) proficiency testing;
b) interlaboratory comparison tests.

In addition, in accordance with the Order of the Ministry of economic development № 326 May 30, 2014, that approves the accreditation criteria, it is provided to carry out the interlaboratory comparison tests, to use certified reference materials and (or) internal quality control, to provide repeated tests. According to the Federal accreditation service laboratories have to confirm their competence using the ICT within 5 years for the accreditation area.

The D.I. Mendeleev Institute for Metrology (VNIIM) has the accreditation certificate of proficiency testing providers № AAC.PTP.0029 issued on 25.10.2019 by the AAC “Analytics” that is the member of ILAC(International Laboratory Accreditation Cooperation) and APLAC (Asia Pacific Laboratory Accreditation Cooperation).

VNIIM is a recognized coordinator of the ICT in various fields. The calorimetric laboratory organized the annual ICT in the control area of quality parameters of coals and fuel oil. 20 rounds of ICT of coals samples (parameters: energy of combustion (gross calorific value), total sulphur content, ash content, volatile matter, hydrogen content) and 15 rounds of ICT of fuel oil samples (parameters: gross calorific value, flash point, density, kinematic viscosity, sulphur content, pour point, ash content) have been conducted over the past 20 years.

Participation in the ICT is appropriate for laboratories that test the quality parameters of fuels used in fiscal measurement in order to assess the measurement results correctness and accuracy.

The results of twenty-year practice of conducting interlaboratory comparison tests on samples of coal and fuel oil are presented.

The ICT rounds, mentioned above, are usually attended by research laboratories of the fuel and energy complex (FEC), coal mines, open-pit mines, oil refineries, research institutes and testing centers in Russia, as well as foreign laboratories in Latvia, Estonia, Ukraine, Belarus, Kyrgyzstan, and Kazakhstan.

The calorimetric laboratory prepares control samples (CS) in such a way that gives opportunity to vary the characteristics of coals and fuel oil from round to round. Assigned value of gross calorific value is traced to the State Primary Standard of the Units of Energy of Combustion, Specific Energy of Combustion and Volumetric Energy of combustion GET 16, which is located in the Laboratory of Calorimetry of D.I. Mendeleev Institute for Metrology. The uncertainty of the assigned value is characterized by the measurement uncertainty of the State Primary Measurement Standard of units of energy of combustion GET 16.

Assigned values of the other parameters are determined during the statistical analysis of the results of the ICT. These values are obtained according to 7.7 of GOST R 50779.60 (similar to 6.2 of GOST R ISO 5725-5), as a robust average of the results reported by all participants in the round of ICT.

Statistical processing of ICT results is carried out in accordance with the requirements of following reference documents: RMG 103, GOST R 50779.60, GOST R ISO 5725-5 and GOST R ISO 5725-6.

Analysis of data, presented by participants of ICT, includes the quality assessment of test results using z-index.

Analysis of the results of all the rounds of ICT carried out over the last 20 years showed a growing interest of laboratories in this type of activity (fig. 1). This interest is demonstrated in the long-term participation of the same laboratories, as well as in appearance of the new participants. The analysis showed the quality improvement of measurements of all coal and fuel oil parameters (table 1).

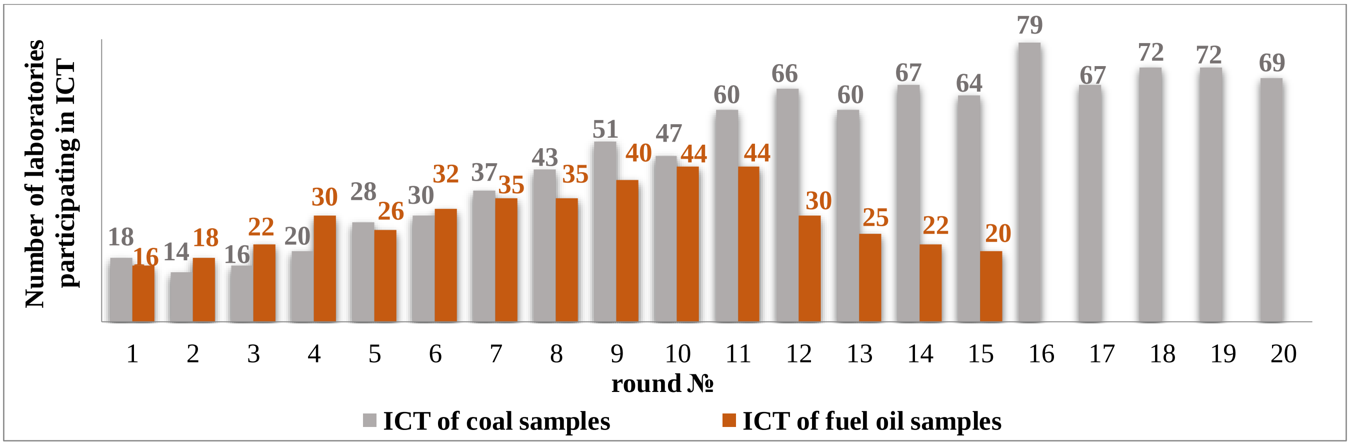

Fig. 1. Laboratories participating in ICT of coal and fuel oil samples

As it can be seen from the table above the number of laboratories with unreliable results of quality parameters is reduced every year (for example, measurements of gross calorific value have changed from ~30 % in the 1st round on a coal sample to less than 10 % in last rounds). At the same time, it is important to mention that unacceptable results are usually represented by new participants. The number of new participants is from 5 to 10 percent of the total number of participants in each new round.

Table 1 - The measurement results of participants of ICT of coal and fuel oil samples

Parameter	**Number of laboratories with unreliable results of measurements of quality parameters of coal samples (in % of total number of laboratories participating in the ICT)**																			
ICT of coal samples																				
Round №	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Gross calorific value	33	21	31	25	29	21	8	12	16	4	7	3	7	6	0	0	1	7	1	0

Parameter	**Number of laboratories with unreliable results of measurements of quality parameters of coal samples (in % of total number of laboratories participating in the ICT)**																			
ICT of coal samples																				
Round №	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Ash	5	0	0	0	1	0	0	0	4	0	2	1	0	0	2	0	0	0	0	1
Sulphur	11	0	0	0	0	0	0	14	0	4	0	5	3	4	2	0	7	7	0	1
Volatile matter	44	21	38	5	14	28	3	6	13	0	24	0	4	5	13	13	7	5	3	2
ICT of fuel oil samples																				
Round №	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**					
Gross calorific value	12	0	5	22	0	0	3	0	0	3	0	0	5	0	0					
Sulphur	6	5	9	3	0	3	3	0	3	2	9	8	5	5	6					
Density	44	22	36	28	12	19	12	18	15	24	15	8	14	10	17					
Flash point	0	11	0	8	4	6	—	6	5	5	21	4	6	—	—					
Kinematic viscosity	0	17	10	0	0	6	0	0	19	4	6	0	0	0	0					

REFERENCE

1. RMG 103 State system for ensuring the uniformity of measurements. Proficiency testing of test (measurement) laboratories, conducting the tests of substances, materials and environmental objects (for composition and physico-chemical properties) by means of interlaboratory comparisons.
2. GOST R 50779.60-2017 (ISO 13528:2015) Statistical methods. Use in proficiency testing by interlaboratory comparison.
3. GOST ISO/IEC 17025 General requirements for the competence of testing and calibration laboratories.

VERIFICATION OF PURCHASED PRODUCTS, INCLUDING REFERENCE MATERIALS, IN ACCORDANCE WITH GOST ISO / IEC 17025-2019

Olga V. Kozlova

CHOU DPO «Educational center "Sodeistvie»
e-mail: olgakozlova3@yandex.ru

Keywords:General requirements for laboratory competence, laboratory resource management, risk assessment, valid test results, reference materials, traceability, metrology

It is impossible to imagine a modern laboratory that does not have the resources appropriate to its field of activity. Most often, laboratories use products and services that are intended only for use in their own laboratory activities or to support the operation of the laboratory. However, in some cases, the laboratory is an intermediary and provides the customer with products or services from an external supplier.

This raises a number of questions for the laboratory: How should the laboratory organize the management of products and services so that it always uses suitable test products? how to avoid the risk of non-conforming products and services in the laboratory that apply to this type of laboratory activity?

The answer to these and other questions helps to find a new version of the interstate standard GOST ISO / IEC 17025-2019 [1], which was introduced in the Russian Federation in September 2019.

Compared to the previous version of the standard, GOST ISO / IEC 17025-2019 [1], in addition to the requirements for determining the requirements for purchased resources and assessing their compliance before use, introduces additional requirements to increase the laboratory's confidence in obtaining suitable purchased resources:

- informing suppliers about their requirements regarding the characteristics of products and services, acceptance criteria, the competence of personnel performing the services, etc .;
- the use of such a tool as risk assessment in laboratory activities.

From the point of view of risk assessment, the absence in the laboratory of a procedure for assessing the suitability (verification) of products and services prior to their use in laboratory activities, with a high degree of probability, can lead to the most serious consequences, including obtaining an unreliable result and, as a result, financial losses.

The verification procedure for products and services, including reference materials, begins with the definition and documentation of the laboratory's resource requirements. The laboratory develops documentation rules independently based on the internal and external context, including being guided by the requirements of GOST ISO / IEC 17025-2019 [1]. The criteria and result of evaluating the suitability of products and services will depend on how fully the laboratory defines the requirements for each resource used. For example, requirements for reference materials, their manufacturers, the content of passports / certificates are contained in GOST ISO / IEC 17025-2019 [1]. Federal Law No. 102-FZ of 26.06.2008 "On Ensuring the Uniformity of Measurements" [2] contains requirements for reference materials used in measurements in the field of state regulation. Requirements for the metrological characteristics of reference materials can be contained in the measurement procedures.

Further actions of the laboratory, consisting in conducting verification and documenting its results, as well as identifying the status of purchased products in the laboratory, should be described in the laboratory's CM documents, accessible, feasible and understandable to all participants in laboratory activities.

The verification results are used in the future when assessing external suppliers in accordance with the requirements of the standard.

Thus, guided by the provisions of the new edition of the standard, in order to eliminate or minimize the risk of using nonconforming products and services, the laboratory must update its documentation containing requirements for specific laboratory resources, procurement procedures and verification of products and services.

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2. Federal Law dated 26.06.2008 No. 102-FZ "On ensuring the uniformity of measurements". Collected Legislation of the Russian Federation, N 26, 30.06.2008, Article 3021.

DEVELOPMENT OF REFERENCE MATERIALS OF COMPOSITION AT JSC IRGIREDMET

Svetlana A Kozlova, Anna V. Zelenkova, S.V. Prokopyeva

Joint-stock company “Irkutsk Research Institute of Precious and Rare Metals and Diamonds”, Irkutsk, Russia
e-mail: kozlova@irgiredmet.ru; av@irgiredmet.ru; analytic@irgiredmet.ru

Keywords: reference materials of composition, certification, metrological characteristics, interlaboratory test, ore, ore processing product, gold, silver

Requirements for accuracy of analytical works in regard to prospecting, exploration, mining and processing of ores are constantly increasing. It can be explained by a variety of factors including the application of international codes prescribing to exploration and mining companies special procedures of quality assurance/quality control of analytical works, along with national regulations. Both international and national regulations are often required to be applied simultaneously. Moreover, recent advancements have expanded the knowledge of ore formation theory; ore processing technologies and standards for the efficiency of technological processes have also evolved. Strict requirements for measurement traceability are imposed on laboratories accredited in the national system (Section 6.5 of GOST ISO/IEC 17025-2019 [1] and Section 23.21 of the Accreditation Criteria [2]).

However, the nature of objectives, functions and objects of analytical works in mining has not changed. Hence, the introduction of specific features and requirements are driven by the necessity of determination of a wide range of test elements contained in samples with different compositions, analysis of a vast amount of run-of-mine samples (i.e. thousands of samples) at a short time without compromising accuracy of measurement results. Conversely, advancements in mining have resulted in a growing market competition among analytical laboratories, rapid developments in measurement instruments and sample preparation equipment, the emergence of new highly-sensitive measurement methods.

In connection with the above, the application of reference materials (RM) of composition for accuracy and traceability of measurement results in mining is increasing every year. For example, JSC Irgiredmet has developed and produced over 350 reference materials of composition of ores and ore processing products, gold-bearing ion-exchange resins and active carbons, precious metal ions since 1980s. All reference materials comply with the requirements of applicable development and production regulations and the quality management system with due regard to the provisions of GOST ISO Guide 34-2014 [3]. Approved reference materials and industry reference materials developed at JSC Irgiredmet in 2004-2020 (as for November 1, 2020) are presented in Table 1 below.

Table 1. State reference materials (SRM) and industry reference materials (IRM) developed at JSC Irgiredmet in 2004-2020

No.	No. according to the State Register of RMs/Industry Register of FSBI VIMS	RM description	Certified characteristics
1	**2**	**3**	**4**
1	SRM 8429–2003 (MSO 0623:2004; COOMET CRM 0038-2005-RU)	RM of gold ion solution (ZlR)	Gold ions mass concentration, mg/cm^3

1	2	3	4
2	SRM 8430–2003 (MSO 0624:2004; COOMET CRM 0039-2005-RU)	RM of silver ion solution (SrR)	Silver ions mass concentration, mg/cm^3
3	SRM 8431–2003 (MSO 0625:2004; COOMET CRM 0040-2005-RU)	RM of platinum ion solution (IV) (PlR)	Platinum ions mass concentration, mg/cm^3
4	SRM 8432–2003 (MSO 0626:2004; COOMET CRM 0041-2005-RU)	RM of platinum ion solution (II) (PdR)	Palladium ions mass concentration, mg/cm^3
5	SRM 8634-2004	RM of gold-bearing ore composition (RZS-04)	Gold mass fraction, ppm (g/t); silver mass fraction, ppm (g/t)
6	SRM 10783 -2016; SRM 10784-2016	RM of gold mass fractions in active carbon (ZAU-1; ZAU-2)	Gold mass fraction, %
7	SRM 10785-2016	RM of gold mass fractions in active carbon (ZAU-3)	Gold mass fraction, %; silver mass fraction, %
8	SRM 10786-2016; SRM 10787-2016; SRM 10788-2016	RM of gold mass fractions in resin (ZIS-1; ZIS-2; ZIS-3)	Gold mass fraction, %;
9	SRM 10888-2017	RM of copper concentrate of copper-zinc ore (KM-RMTz)	Copper mass fraction, %; gold mass fraction, ppm (g/t); silver mass fraction, ppm (g/t)
10	SRM 11134-2018; SRM 11135-2018; SRM 11136-2018	RM of Sari Gunay deposit’s gold-bearing ore composition (RZSG-1; RZSG-2; RZSG-3)	Gold mass fraction, ppm (g/t); silver mass fraction, ppm (g/t); copper mass fraction, %; arsenic mass fraction, %; mercury mass fraction, %
11	SRM 11342-2019; SRM 11343-2019; SRM 11344-2019; SRM 11345-2019	RM of Verkhneye Kayratinskoe deposit’s tungsten ore composition (RVSK-1; RVSK-2; RVSK-3; RVSK-4)	Tungsten oxide mass fraction (IV), %; bismuth mass fraction, %; molybdenum mass fraction, %; copper mass fraction, %
12	IRM No. 911-19; IRM No. 912-19; IRM No. 913-19; IRM No. 914-19; IRM No. 915-19	RM of gold-bearing ore composition (IRG-27-2018; IRG-28-2018; IRG-29-2018; IRG-30-2018; IRG-31-2018)	Gold mass fraction, ppm (g/t); arsenic mass fraction, %; total sulphur mass fraction, % sulphide sulphur mass fraction, %; total carbon mass fraction, % organic carbon mass fraction, %
13	IRM No. 936-19; IRM No. 937-19; IRM No. 938-19; IRM No. 939-19	RM of gold- and silver-bearing ore composition (IRG-41-2019; IRG-42-2019; IRG-43-2019; IRG-44-2019)	Gold mass fraction, ppm (g/t); silver mass fraction, ppm (g/t)
14	IRM No. 986-20; IRM No. 987-20; IRM No. 988-20; IRM No. 989-20	RM of composition of gold-processing plants’ technological products (IRG-61-2019; IRG-62-2019; IRG-63-2019; IRG-64-2019)	Gold mass fraction, ppm (g/t); silver mass fraction, ppm (g/t); arsenic mass fraction, %; antimony mass fraction, %; iron mass fraction, %; total sulphur mass fraction, %; sulphide sulphur mass fraction, %; total carbon mass fraction, %; organic carbon mass fraction, %

In recent years, customers have been showing increasing interest to JSC Irgiredmet’s RMs of composition of base and gold-bearing ores and ore processing products, obtained from customer’s or in-house materials. Upon such requests, JSC Irgiredmet has developed, certified and produced reference materials of composition for a total weight of 9 tons in 2018-2020. Mass fractions of various elements have been certified including gold, silver, copper, iron, lead, arsenic, total sulphur, sulphide sulphur, total carbon, organic carbon and some other elements in a wide range of content.

For example, the certified mass fractions of gold, silver and lead vary from 0.015 to 125 ppm (g/t), from 1.32 to 12,735 ppm (g/t), and from 0.0065 to 35.9%, correspondingly.

The following reference materials have been developed, certified and produced at JSC Irgiredmet in 2018-2020:

– 7 approved reference materials (gold-bearing ore, tungsten ore);

– 13 industry reference materials (gold-bearing ore, gold- and silver-bearing ore, technological products of gold-processing plants);

– 63 plant reference materials (gold-bearing ore, base-metal ore, ore processing products);

– several dozens of approved reference material sets (precious metal ion solutions, the total amount is approximately 12,000 of ampoules with a volume of 5 cm^3).

Currently, JSC Irgiredmet holds contracts for the development of 5 industry reference materials of composition of ore processing products and approximately 30 plant reference materials of gold-bearing ores and ore processing products. Also, the documentation for the development of 2 reference materials of composition of ores certified and tested for gold and silver is undergoing metrological examination and will be submitted to Rosstandart for approval. The development of reference materials of composition of geological and technological samples at JSC Irgiredmet will be continued.

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OVERVIEW OF STATUTORY BASIS FOR WORKS ON REFERENCE MATERIALS

Olga N. Kremleva, Sergei V. Medvedevskikh, Egor P. Sobina

UNIIM – Affiliated Branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
ORCID: 0000-0001-8489-2437, e-mail: 251@uniim.ru
ORCID: 0000-0002-6003-040X, e-mail: kremleva@uniim.ru
ORCID iD: 0000-0003-3084-1612, e-mail: uniim@uniim.ru

Modifications to the main law of the Russian Federation on assurance of measurement uniformity came into force in 2020 (Federal Law №102-FZ dated 26 June 2008 “On assurance of uniformity of measurement”). The modifications resulted in a number of new bylaws including within in the frame of works on reference materials. At the same time there is a number of international documents with requirements and guidelines for development and appliance of reference materials.

The report provides overview of fundamental principles of legislative acts in the field of measurement uniformity assurance. The summary on modifications concerning procedures on development and certification of types and application of reference materials in sphere of state regulations are presented.

The next principles of legislative acts are considered:

— Federal Law №102-FZ dated 26 June 2008 “On assurance of uniformity of measurement” (ed. Federal Law №496-FZ dated 27 December 2019);

— Resolution of the Government of the Russian Federation №734 dated 23 September 2010 “On standards of units used in the sphere of state regulation of assurance of the uniformity of measurements” (ed. Resolution of the Government of the Russian Federation №1355 dated 21 October 2019);

— Order of the Ministry of industry and trade of Russia dated 11.02.2020 No. 456 "On approval of requirements to the contents and construction of the state verification schemes and local verification schemes, including their development, approval and change; requirements to registration of materials for primary certification and periodic scheduled certification of measurement units standards used in the field of state regulation of assurance of uniformity of measurements; forms of the certificate about certification of the standard of unit; requirements for registration of rules for the content and application of the standard of unit; the form of notification of the unsuitability of the standard of a unit for its application»;

— Order of the Ministry of Industry and Trade of the Russian Federation №2906 dated 28 August 2020 “On approval of the procedure for founding and maintaining the Federal Information Fund for assurance of the uniformity of measurements, transmitting information to it and making changes to this information, and providing documents and information contained therein”;

— Order of the Ministry of industry and trade of the Russian Federation №2907 dated 28 August 2020 “On approval of the procedure for establishing and changing the interval between calibrations of measuring instruments, the procedure for establishing, canceling calibration methods and making changes to them, requirements for calibration methods of measuring instruments”;

— Order of Federal Agency on Technical Regulating and Metrology №1404 dated 17 August 2020 “On amendments to the Administrative regulations on the provision by the Federal Agency for Technical Regulating and Metrology of state services for approving the type of reference materials or the type of measuring instruments, approved by order of the Federal Agency for Technical Regulating and Metrology № 2346 dated 12 November 2018 No. 2346”;

For participants information the summary of activities of State Service on Reference Materials for composition and properties of substances and materials is presented.

CORRELATION OF TEST RESULTS OF A CHEMICAL COMPOSITION AND HUMAN ERRORS

Ilya Kuselman

Independent Consultant on Metrology, Modiin, Israel
e-mail: ilya.kuselman@gmail.com

One of the problems in testing chemical composition of a multicomponent substance, material or object is a correlation of test results. A number of chemical analytical techniques are used to overcome possible correlations between measured values. These techniques include extraction of analytes from a sample and chromatographic separation of an analyte from other components of the sample. Chemometrics software is applied for separation of spectral signals. Sample digestion and standard additions of an analyte to a sample are used for calibration of a measurement system overcoming multiplicative matrix effects of a sample, and so on. Therefore, correlations arisen in the measurement process should be in general negligible and test results for two or more components metrologically-independent.

However, human activity is never free from errors. In chemical analysis human errors may lead as to correlation of test results, as to incorrect evaluation of the tested properties. Therefore, study and reducing human errors is necessary in analytical chemistry at validation of standard operation procedures, and required from the laboratories seeking accreditation.

At the same time, test results of a chemical composition are inevitably correlated when their actual (‘true’) values are correlated. Correlations of contents of different sample components may be caused, for example, by stoichiometry of native compounds (in geological, environmental and other samples) and technological reasons in the production of some artificial materials (alloys, drugs, food, etc.).

When components of a substance or material are subject to a mass balance constraint (sum of their mass fractions, mole fractions or any other positive quantity ratios is 100 % or 1), test results of the components’ contents are termed “compositional data”. These data are correlated because of the constraint, and the relevant correlations are referred to as “spurious”.

Any correlation of test results should be taken into account as able to influence understanding a chemical composition and evaluation of risks in conformity assessment of a substance, material or object.

ASTIMATION OF HOMOGENEITY BISMUTH-CONTAINING GLASSY REFERENCE MATERIFLS

Valentin A. Kutvitskiy, Valentina V. Borisova, Elena V. Mironova, Inna A. Romanova

MIREA – Russian Technological University (RTU MIREA), Moscow, Russia
ORCID iD: 0000-0003-4701-5288, e-mail: vv_borisova@mail.ru

Keywords: bismuth-containing glassy samples, homogeneity of composition and properties, X-ray spectral microanalysis, microhardness

Modern express methods of analytical control are widely used monitoring the quality of oxide materials. However, the possibilities of these methods are currently limited by lack of versatile homogeneous reference materials for comparison purposes. Such reference materials can most effective be produced by vitrification methods. In this connection, glassy reference materials based on bismuth-borate systems are of great interest.

Glassy samples were obtained using a bismuth-borate matrix by melting it at T = 1273-1373K. Afterwards, the melt was poured into a crucible. After the completion of the vitrification process, the samples were subjected to post-hardening annealing at a temperature of 673 K for 12 hours. Defined elements introduced into the composition of the samples in the form of individual oxides or oxide materials. According to the described technology, glassy samples containing 70 wt % Bi_2O_3, (30-X-Y) wt %, B_2O_3, X (0-3%) wt % MoO_3, Y (0-24%) wt % GeO_2 were obtained.

To use the synthesized bismuth-containing samples as reference materials in spectral analysis methods, it was necessary to assess their quality. Namely, it was necessary to evaluate a set of physical characteristics that can affect the metrological parameters of measurements made with their use. In order to characterize a reference material candidate, it is necessary to establish the following: synthesized samples are glasses, they are structurally homogeneous, and the distribution of substances in the sample volume is homogeneous.

The glassy state of the bismuth-containing samples was established by visual analysis of the fracture and crystal-optical analysis. The final conclusion was made based on the results of X-ray Phase Analysis (DRON-3M diffractometer, Burevestnik, Russia). Any reflections indicating the presence of long-range order in the structure of the sample were absent in the obtained diffraction patterns. In addition, the isotropy of the samples and the absence of pronounced peaks in the diffractogram allowed us to conclude that there are no microcrystallites in the volume of the sample [1].

The structural and component homogeneity of distribution in the volume was judged by the results of X-ray Spectral Microanalysis (X-ray microanalysis). The studies were carried out on a JXA-3A two-channel X-ray spectrometer (an electron gun with a tungsten cathode, an accelerating voltage of 35 keV, anode current of 20 mA, the diameter of the electron probe did not exceed 3 µm, and a LiF analyzer crystal). The intensities of the secondary X-ray radiation of the determined elements were measured at various points of the sample, or the intensities of the secondary radiation of one of the elements were measured by scanning the electron beam over the surface of the sample. To assess the homogeneity characteristics of glassy bismuth-containing samples, the obtained data were processed according to the algorithm described in GOST 8.531 [2].

Glass quality is often judged by mechanical properties. To assess the homogeneity of bismuth-containing glassy samples, we used the microhardness index. The microhardness of the samples was judged by the size of the indentation when a square diamond pyramid with an angle between the faces of 136° and a load of 200 g was pressed into the glass [3]. Its value was 450-490 N/mm^2. The measurements were carried out on a PMT-3 microhardness tester (LOMO, Russia). The metrological characteristics of the technique were preliminarily determined from the results of measuring the values of the microhardness of NaCl crystals according to [4]. Eighteen samples were tested in 12 areas for each sample and 7 measurements in each area. The intra-instance and inter-instance homogeneity of glassy bismuth-containing samples was estimated according to the algorithm established in [2, 5] based on the results of microhardness measurements.

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OVERVIEW AND ANALYSIS OF THE INDUSTRY BASE OF CRM INCLUDED IN THE INDUSTRY REGISTER OF CRMs ACCEPTED (RECOMMENDED) FOR APPLICATION IN LABORATORY ANALYTICAl SUPPORT OF GEOLOGICAL EXPLORATION FOR SOLID MINERALS

Maria I. Lebedeva, Alexey Yu. Kit

All-russian scientific-research institute of mineral resources named after N.M.Fedorovsky, Moscow, Russia
e-mail: LebedevaMI@vims-geo.ru

Ensuring the quality of laboratory research of mineral raw materials, which is currently understood as the compliance of the results of mineralogical and analytical work to presenting (established) requirements for their completeness and reliability [1], is one of the primary and priority tasks at all stages of geological exploration.

A system which has received the name abroad «QA/QC» (Quality Assurance Quality Control of assay data) is used to control the stages of the data acquisition process. The system controls the stages of sampling, preparation, analysis of samples and maintenance of databases, including:

– selection of duplicates and formation of group samples;
– transfer of samples to the laboratory and organization of sample preparation;
– measurement method and quality of performed studies;
– work with databases [2].

Analysis of foreign practice shows that in projects with a high level of confidence, the quantity of QA/QC samples varies in the range from 15% to 25% of the total quantity of analyzed samples, 6% of which are CRM.

For many years in the geological industry of our country there has been an industry-specific Quality Management System for analytical work - UKAR (analogous to foreign QA/QC [2]), which covers all stages of laboratory research from sampling to quality control of analysis, including requirements for analysis methods and reference materials of the composition. Over the years, a significant contribution to the implementation of the listed aspects of ensuring the reliability and comparability of laboratory research has been made by VIMS, which acts as the Federal Scientific and Methodological Center for Laboratory Research and Certification of Mineral Resources of the Ministry of Natural Resources of Russia.

The Institute is a metrological service in the sphere of responsibility of “Rosnedr” for ensuring the uniformity of measurements, the competence of which is confirmed by accreditation in the Federal Service for Accreditation (“RUSACCREDITATION”) for the right to carry out work in the field of ensuring the uniformity of measurements, in terms of attestation of procedures (methods) of analysis and metrological examination of documentation (accreditation certificate No. 01.00115-2013). As part of the metrological support of the industry, work is being carried out on the production of reference materials (CRM) of various types of solid minerals, as well as a procedure for extending the validity period of CRM in the industry-specific CRM and in-house reference standards categories based on the results of assessing the stability of the metrological characteristics of CRM [3-5]. FSBI "VIMS" is accredited in accordance with the requirements of the International Standard ISO Guide 34: 2009 (ISO Guide 34), which confirms the technical competence and functioning of the quality management system of the manufacturer of reference materials in terms of CRM production (accreditation certificate No.AASRM.00190). The Institute has all the necessary resources to carry out a full range of works on the production of CRM, including the scientific potential accumulated over many decades of the Institute's existence, modern technical equipment and successful cooperation with the leading analytical laboratories of the industry (Figure 1).

Fig. 1. CRM of FSBI «VIMS»

In order to implement a unified scientific and technical policy and provide methodological assistance to laboratories and subsoil users of the geological industry [6, 7], an Industry register of reference materials approved (recommended) for use in laboratory and analytical support of geological exploration for solid minerals has been created and is maintained (Register of CRM).

Inclusion in the Industry Register is carried out on the basis of a positive conclusion on compliance with industry requirements based on the results of a metrological expert examination.

The Register of CRM contains the following sections:

- GSO (CRM of approved types). Section I: «State CRM»;
- OSO. Section II: « Industry-specific CRM»;
- SOP. Section III: «In-house reference standards »;
- MSO. Section IV: «International CRM of the composition and properties of substances and materials of the states-parties of the agreement».
- Information data on expired CRM.

130 CRM were approved in the categories of OSO and SOP in 2019, of which 48 were developed by FSBI «VIMS». Information on the CRM approved in the OSO and SOP categories in 2019 are presented in Table 1.

Table 1

Designer	Type of CRM	Quantity of designed CRM	Category of CRM
FSBI «VIMS»	ferrous metal ores and products of their processing	1	OSO
		25	SOP
	Non-ferrous metal ores and products of their processing	1	OSO
	polymetallic ores	8	OSO
		3	SOP
	precious metal ores	10	SOP
ORE Research & Exploration Pty Ltd (Australia)	precious metal ores and products of their processing	20	OSO
ROCKLABS (Australia)	precious metal ores and products of their processing	13	OSO
JSC "Krastsvetmet"	precious metal ores and products of their processing	4	SOP
	precious metal alloys (incl. technical products)	12	
LLC "NTC "Minstandart "	precious metal ores	13	OSO
JSC "Irgiredmet"	precious metal ores	9	OSO
		4	SOP
LLC "Svetloe"	precious metal ores	4	OSO
OJSC "KGILTS"	earth's formations	3	OSO

As of the end of the Q3 of 2020, the CRM Register is represented by 997 reference materials approved (recommended) for use in laboratory and analytical support of geological exploration for solid minerals (Fig. 2), 98 CRMs of which are samples of foreign production (ROCKLABS LTD (Australia), ORE Research & Exploration Pty Ltd (Australia)).

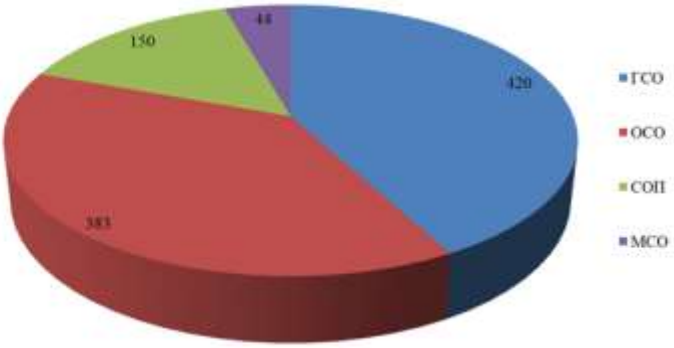

Fig. 2. Diagram of the distribution of CRM by categories in the Register of CRM
(from top downward: GSO, OSO, SOP, MSO)

A comparative diagram of the condition status of the Register of CRM for 2017-2020 is presented at Figure 3.

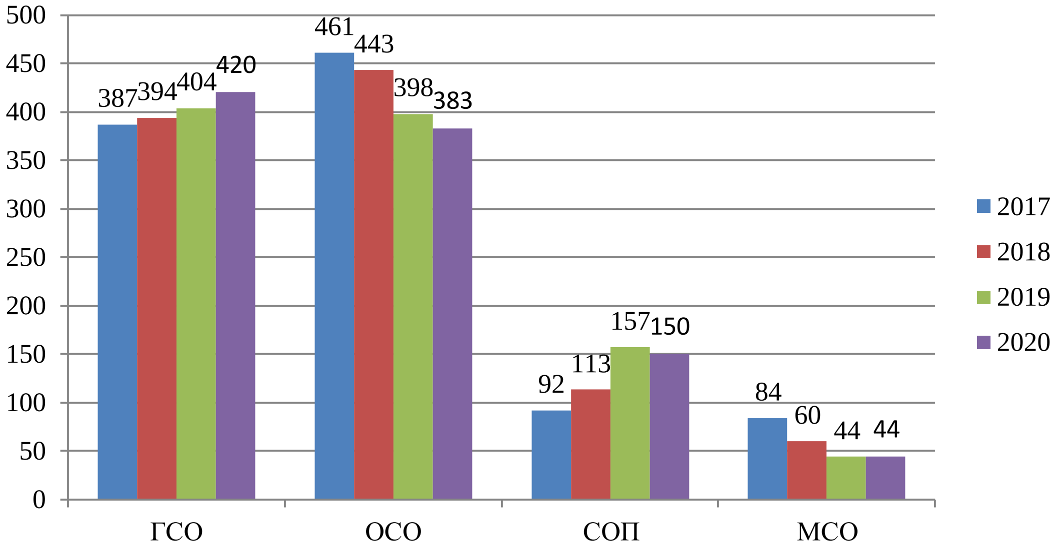

*Fig.3.*Condition status of the Register of CRM for 2017-2020

There is a trend towards a reduction in the nomenclature of OSO category CRM and an increase in the number of SOP category samples. This circumstance is due to the fact that the customers of the development of CRM (they are currently mainly the subdivisions of organizations – laboratories, geological services, factories that search, develop and process ores containing precious metals) are trying to reduce the cost of services provided to them and order the development of SOP.

Information on the composition (type) of CRM for each category is presented in the form of a diagram (Figure 4). The presented data show that:

- samples of the GSO category are mainly represented by CRM of composition of precious metal alloys (50,5%), earth's formations (15.8%), ores of precious metals and products of their processing (9.9%), ores of ferrous metals and products of their processing (7.9%);

- samples of the OSO category are mainly represented by CRM for the composition of precious metal ores and products of their processing (66.8%), as well as earth's formations (18.6%);
- samples of the SOP category are mainly represented by CRM for the composition of precious metal ores and products of their processing (64.4%), as well as products of processing of ferrous metal ores (15.9%);
- samples of the MSO category (44 CRMs) are mainly represented by CRM for the composition of non-ferrous metal ores and products of their processing (34.2%), ferrous metal ores and products of their processing (31.9%), precious metal ores and products of their processing (15.7 %), earth's formations (9.0%).

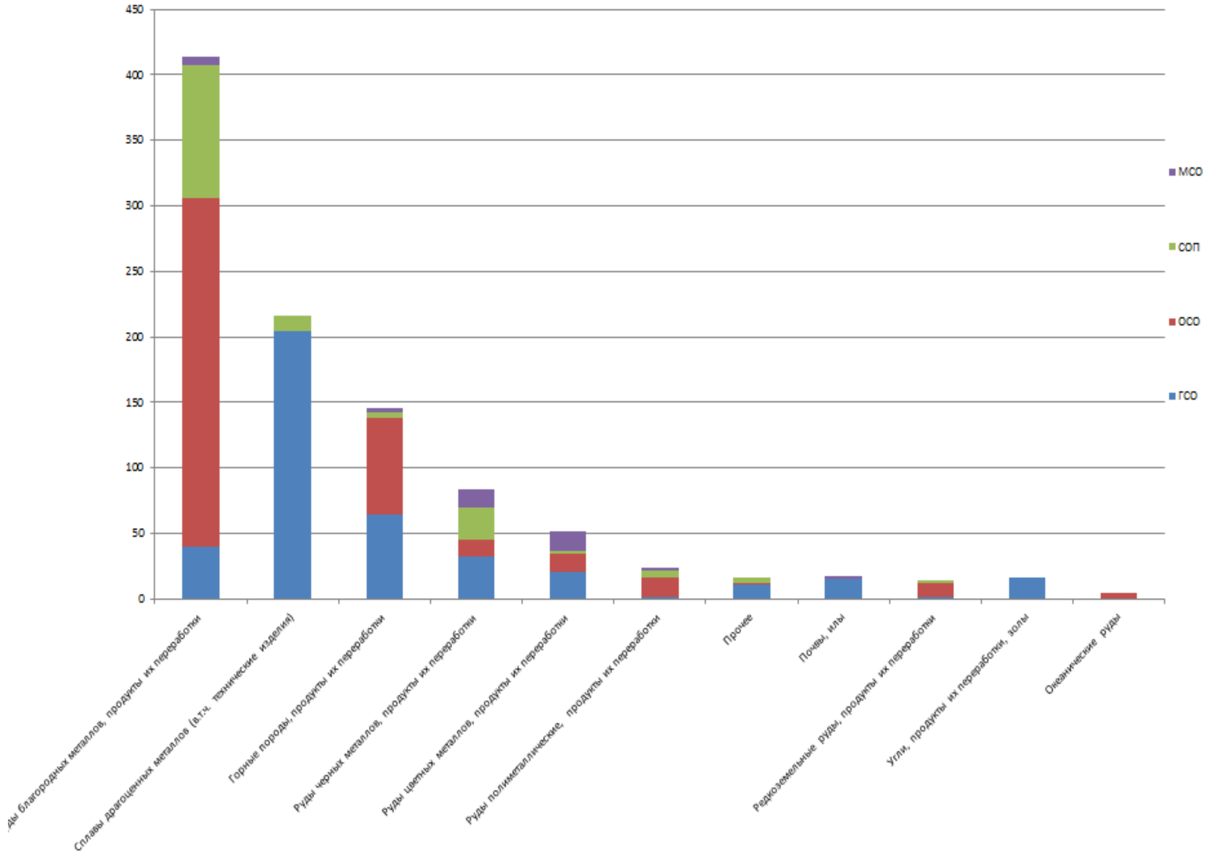

Fig. 4. Nomenclature of the Register of CRM by types and categories

In order to extend the shelf life of CRM, the metrological service of FSBI "VIMS" received justification applications, as well as documents containing information on the assessment of the stability of the values of metrological characteristics of 17 CRM. After the metrological examination, the shelf life of the samples was extended.

Up-to-date information is presented on the website of FSBI "VIMS" (vims-geo.ru) in the section "Industry register of CRM".

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UNUSUAL USE OF THE STANDARD SAMPLE COMPOSITION OF BLOOD CONTAINING MERCURY (GSO 9653-2010)

Malov A.M., Ŝegolihin D.K., Sibiryakov V.K.

«Institute of Toxicology» of the Federal Medico-Biological Agency, Saint Petersburg, Russia
ORCID: 0000-2192-3042, e-mail: malexmish@rambler.ru

Key words: standard sample GSO 9653-2010, mercury, blood, lyophilisate, pyrolysis

Increasing the sensitivity of methods of analysis and their accuracy are current trends in the development of analytical chemistry. This fully applies to the determination of toxic metals in biological samples, especially in blood as a common environment for the whole organism. Data on the content of mercury in the blood of patients is a diagnostic sign of intoxication.

One of the most effective ways to solve this problem is the use of direct analysis methods that do not involve sample preparation of the material - physical impact, the addition of various reagents, etc. Such preparation is necessary for biological samples with a complex matrix, such as blood, consisting of liquid plasma and formed elements of a complex chemical composition.

In recent years, a method of pyrolytic atomization of mercury has been developed and applied. The bound mercury contained in the biological sample is converted into an atomic state by pyrolysis in an atomizer (pyrolytic attachment). Then atomic mercury is transferred from the atomizer to the analytical cell by the carrier gas (air). This study was carried out on domestic mercury analyzers RA-915 and Julia 5K with appropriate pyro-attachments.

The development of this method was the use of blood lyophilisate for pyrolysis, obtained by low-temperature vacuum drying (less than -50 ° C, and below 0.035 mbar), instead of liquid blood containing only about 20% of dry matter. This technique made it possible to exclude the aqueous phase and increase the amount of biomaterial introduced into the pyrolysis furnace [1].

An extremely important role for the analysis results is played by the use of an adequate standard sample, which allows the relative values obtained on the analyzer to be converted into the absolute concentrations of the analyte in the biomaterial. In the FSBIS IT of FMBA of Russia reference materials of blood composition have been developed, containing such metals as lead, mercury, cadmium, beryllium, thallium - GSO 9104-2008, GSO 9653-2010, GSO 10128-2012, GSO 10129-2012, GSO 10236, which are lyophilisates blood with a known content of the analyte [2].

Mercury occupies a special place among these metals, both as a toxicant and as a subject of analysis; special attention is paid to the study of this analyte. In the proposed method for the analysis of mercury in blood, it is proposed to use reference materials of blood composition containing mercury (GSO 9653-2010,) as a standard material, not in dissolved form, as provided by the standart sample Instruction, but in the form of its lyophilisate. Thus, products of the same state of aggregation and physical and chemical composition but differing in the content of the analyte, are compared. On the basis of weighed portions of the GSO 9653-2010 lyophilisate, a calibration dependence is construct. Weight dosing also contributed to the increase in the reliability of the analysis results, because that is more accurate than volumetric material dosing [3].

As a result of the proposed innovations, it was possible to achieve the sensitivity of the method for determining mercury in the blood of 0.1 μg/dm^3 with an SD of 0.1 μg/dm^3, which meets the highest needs of modern medical and biological analytics.

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HARDWARE AND METROLOGICAL SUPPORT OF POLLUTANTS DISCHARGE CONTROL SYSTEMS

Mary Yu. Medvedevskikh[a], Konstantin A. Karpov[a, b], Viacheslav F. Markov[b, c]

[a] UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
Researcher ID: G-6171-2017, e-mail: lab241@uniim.ru
[b] Ural Federal University named after the first President of Russia Boris Yeltsin, , Ekaterinburg, Russia
[c]Ural Institute of State Fire Service of EMERCOM of Russia, Ekaterinburg, Russia
Researcher ID: G-6171-2017, e-mail: lab241@uniim.ru

Keywords: environmental protection, automatic control of discharges into water bodies, heavy metal ions, semiconductor sensors, control and accounting system of discharges, metrological support, metrological traceability

To implement the provisions of Article 67 of the Federal Law of 10.01.2002 No. 7-FZ "On Environmental Protection" (as amended by the Federal Law of 31.07.2020 No. 298-FZ) [1], which prescribes the organization of automatic control of emissions and discharges of pollutants, specialists in various fields are carrying out theoretical and experimental researches on the creation and implementation of instruments of automatic control and accounting of pollutant emissions and discharges. As well the fixation and transmission to the state register of information about environmentally hazardous pollutant emissions and discharges are taken place.

The Government Decrees No. 262 [2] and No. 263 [3] of 13.03.2019, which have come into force, provide rules of the creation and exploitation of emissions and discharges automatic control systems as well as the requirements for them. According to paragraph 9 of the Government Decree No. 262 [2] stationary discharge sources are included in the program of automatic control system creation when means and methods of pollutants concentration measurement under operating conditions of a stationary discharge source are *available*. Pollutant discharge indexes subjected to automatic control include concentrations of pollutants in waste waters or other indexes which describe quality and safety of waste waters such as pH value, chemical oxygen demand (COD) or biochemical oxygen demand (BOD), volumetric flow and temperature of discharged waste waters described in Information Technology Reference Book (ITS) 22.1-2016 [4] and (or) in ITS of the Best Available Technology (NDT) for specific branch of industry [5–7]. The discharged substances that pose a danger to the environment and humans include, for example, heavy metals (Pb, Cu, Zn, Ni, Cd, Co, Sb, etc.), the sources of which are ferrous and non-ferrous metallurgy, the extraction of solid and liquid fuels, mining and processing complexes, electrical production, etc [8].

Considering a wide range of enterprises and organizations that have stationary sources of discharges and are obliged in the medium term to create and put into operation systems for automatic control of emissions and discharges of pollutants, an urgent task is to create domestic components for automatic control systems, for example, sensors for substances dissolved in water. Selective sensors based on thin films of metal sulfides obtained by Ural scientists by chemical synthesis from aqueous media [9–13] may be promising for the rapid determination of heavy metal ions. The sensitivity of such sensors is explained by surface effects that are not noticeable in macro objects, but which affect the functional properties of two-dimensional objects, such as thin films. The resulting sensors showed lower detection limits for heavy metal ions in comparison with analogs on the market, as well as the ability to determine the required ion in the presence of impurities. Simplicity of design, selectivity, retention of sensitivity and operability in conditions of polluted water and in a wide range of temperatures make it possible to consider thin-film sensors in the hardware design of systems for monitoring discharges of pollutants.

VNIIM-UNIIM, as a national metrological institute, is developing metrological support for automatic measuring and accounting instruments for indexes of emissions and discharges of pollutants, since issues related to the implementation of activities in the field of environmental protection and measurements in the field of environmental protection, for which mandatory metrological requirements have been established, relate to the sphere of state regulation of ensuring the uniformity of measurements in accordance with the Federal Law of 26.06.2008 No. 102-FZ "On ensuring the uniformity of measurements" [0].

In UNIIM – a branch of D.I. Mendeleev Institute for metrology the work in terms of metrological support of discharges into water bodies is being held. The prototype of automatic control and accounting system for pollutant discharges into water bodies has been crated for further purposes:

- calibration (verification) of industrial continuous analyzers designed to control the properties and composition of water;
- conducting tests in order to approve the type of automated measuring systems for industrial environmental control of discharges;
- modeling of the discharge point, design of industrial environmental control systems for discharges and the formation of a report on the results of its implementation.

First of all, the decision was made to model the system and develop metrological support for the facilities of large industrial enterprises. The list of pollutants for which mandatory continuous automatic control is carried out is given in ITRB 8-2015 “Information and technical guide to the best available technologies. Wastewater treatment in the manufacture of products (goods), performance of work and provision of services at large enterprises " [15**Ошибка! Источник ссылки не найден.**]. Among them are heavy metal ions, the concentration of which is planned to be recorded using specially made sensors based on thin semiconductor films of metal sulfides.

When testing individual components of the system, to assess the accuracy characteristics, as well as to ensure the traceability of the results of measuring the characteristics of the water composition, the State secondary standard of units of mass fraction and mass (molar) concentration of components in solid and liquid substances and materials is applied based on the volumetric titrimetric method of analysis State Secondary Standard GVET 176 1–2010 [16], which in turn has metrological traceability to units of quantities reproduced by the State Primary Measurement Standard of units of mass (molar) fraction and mass (molar) concentration of a component in liquid and solid substances and materials based on coulometry State Primary Standard GET 176–2017 [17].

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ZEOLITES – PROMISING CANDIDATE MATERIAL FOR CREATING COMPARISON STANDARDS WITH RECOVERABLE PROPERTIES

Mary Yu. Medvedevskikh., Anastasia V. Kasilyunas

UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
ORCID 0000-0003-3798-9556, e-mail: kasilyunasav@uniim.ru

Keywords: zeolites, molecular sieves, moisture measurement, water mass fraction, humidity, water content, comparison standards, thermogravimetric method

One of the reliable ways to obtain reliable measurement results that meet the traceability requirements is the use of reference material (hereinafter referred to as RM). In the field of moisture metering under conditions of a wide range of analyzed substances, various aggregate states, homogeneity and stability, the practical use of RM developed on the basis of pure substances allows unifying the procedures for monitoring the metrological characteristics of measuring instruments during verification, calibrations, calibrations and tests for type approval purposes.

The mass fraction of water in the same material can vary significantly depending on the temperature and humidity of the environment, storage and transportation conditions, it is characterized by the need to select methods (techniques) for measuring the water content. The objective of this study is to select a suitable candidate substance for the creation of RM with recoverable properties, certified by the mass fraction of water. The main requirements for the physicochemical properties and composition of the candidate material were formulated: the presence of a regular and homogeneous structure, the ability to reversibly hydrate, when heated to 300 ° C, no release of volatile substances other than water and the preservation of basic physicochemical properties, high stability during transportation and storage.

All of the above requirements are best met by materials based on porous substances such as zeolites (trade name - "molecular sieves") - crystalline aluminosilicates containing oxides of alkali and alkaline earth metals, characterized by precise and uniform pore size, which under normal temperature conditions are filled with molecules water. The empirical formula characterizing the composition of a molecular sieve is written as follows

$$Me_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot wH_2O,$$

where Me - alkali metal cation, n - charge (valence) of the cation, x - molar ratio SiO_2 / Al_2O_3 (varies from 2 to infinity), w - mass fraction of water contained in the voids of the zeolite [2, 3].

For research purposes, the most suitable type of molecular sieve was identified - 3A, the diameter of the entrance windows of which is three angstroms (Ȧ) containing in its composition $0.6\ K_2O : 0.40\ Na_2O : 1\ Al_2O_3 : (2.0 \pm 0.1)\ SiO_2 : x\ H_2O$. The fundamental features of zeolite 3A are the presence of a regular porous structure of molecular size, the ability to selectively adsorb and desorb a significant amount of physically bound water molecules and, finally, the reversibility of hydration processes, due to which there is a unique opportunity to control the process of absorption of water molecules by the zeolite by varying temperature conditions until a state of equilibrium is reached. Thus, the ability to restore properties in water provides multiple use of RM based on high-purity substances - zeolites.

In the interests of creating an RM based on zeolite 3A, a step-by-step algorithm was drawn up for several cycles of material studies aimed at establishing (checking) the ability of a molecular sieve to restore its properties in water.

Before filling the inlet cavities and windows of the zeolite with water, it is necessary to activate it - to remove the sorbed vapor-gas mixtures and determine the starting point of the water content. The first stage is vacuum degassing (when the material is heated to 300 °C, it is performed on a thermogravimetric unit). The second stage is to test the hypothesis about the complete release of pores; for this, the method of differential scanning calorimetry and thermogravimetric analysis, coupled with a mass-spectrometer (hereinafter referred to as TGA / DSC-MS), is best suited for this, which allows to control not only the water outlet temperature, but also the chemical composition emitted steam-gas mixture. Both methods are implemented on installations that are part of the State primary measurement standard of mass fraction and mass (molar) concentration of water in liquid and firm substances and materials GET 173-2017 (hereinafter – GET 173) [1].

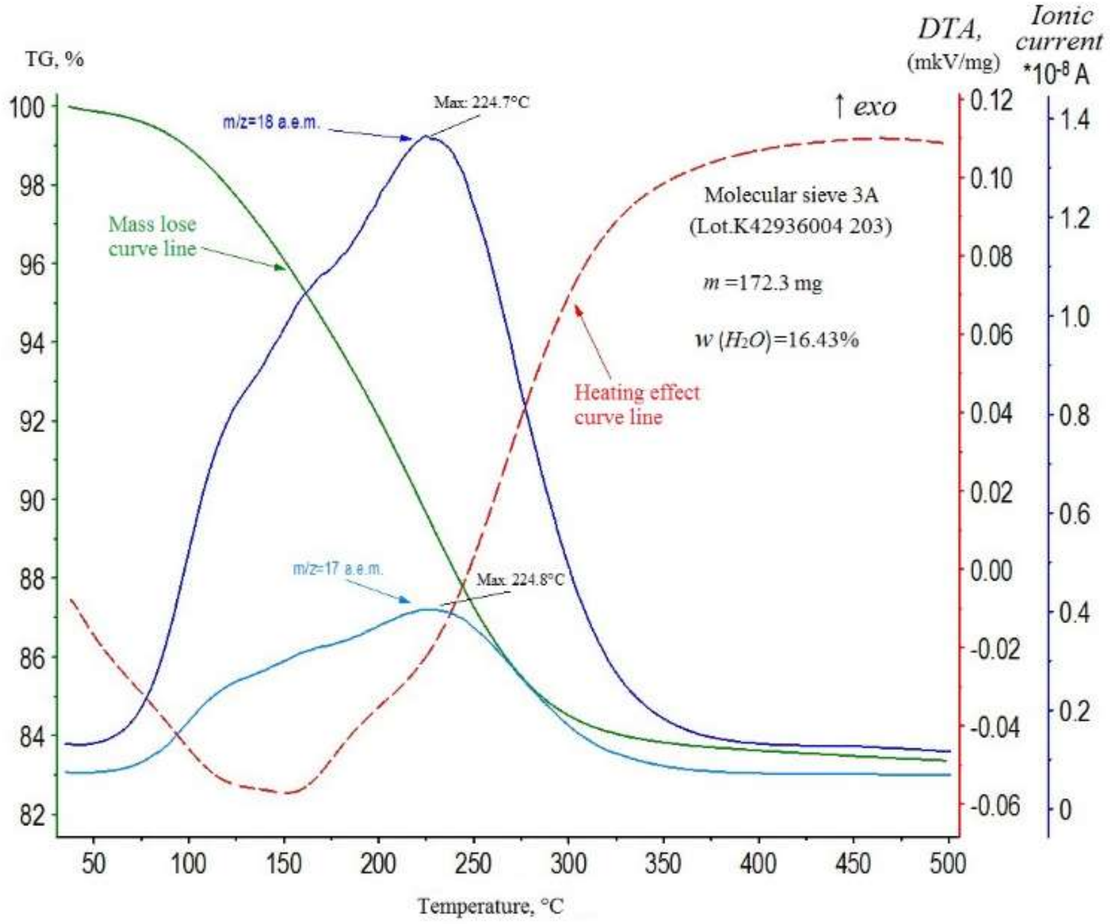

Fig. 1. Thermogram of a molecular sieve 3A

Based on the results of checking the chemical composition of the vapor-gas mixture released during heating of the zeolite by the TGA / DSC - MS method (Fig. 1), it was found that at temperatures from 100 °C to 300 °C water is released (characteristic mass numbers *m.z.* = 17 *a.e.m.*, *m.z.* = 18 *a.e.m.*) and carbon dioxide (*m.z.* = 44 *a.e.m.*). Other compounds were not detected, an increase in temperature up to 500 °C does not lead to a change in mass and visible thermal effects.

The third stage is the study of the kinetics of filling the pores of the material with water and determination of the increase in the mass of the material due to the adsorbed water. Further, the fourth stage is the determination of the pore volume of zeolite by the gas adsorption method, implemented on the State primary measurement standard of specific adsorption of gases, specific surface area, specific pore volume, pore size, open porosity and gas permeability coefficient of solids and materials GET 210-2019 (hereinafter - GET 210) [4]. This algorithm is supposed to carry out several cycles of research.

To date, the first cycle of studies has been completed, and the water content values attainable with complete filling of the pores of zeolite 3A with water, determined by various methods, have been obtained. The results of pore volume measurements obtained on GET 210, when recalculated for filling the entire pore volume of the material with water, are comparable with the results of measurements obtained on GET 173.

In 2020, the second cycle of studies was carried out at GET 173, the maximum moisture capacity (water content when the entire pore volume of the material was filled with water) remained at the same level, which is indirectly confirmed by the preservation of the porous structure and the invariability of the volume of the zeolite pores filled with water.

Consequently, zeolites of type 3A are really a suitable candidate material for creating RM with reducible properties. Currently, studies are being carried out aimed at assessing the homogeneity and stability required for the approval of the RM, as well as the accuracy characteristics, to assess compliance with the requirements of the State Calibration Scheme for measuring instruments for water content in solid and liquid substances and materials [5].

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APPLICATION OF THE LYOPHILIZATION SYSTEM FOR PREPARATION OF REFERENCE MATERIALS FOR COMPOSITION OF NUTRITION PRODUCTS

Mary Yu. Medvedevskikh[1], Natal'ia L. Vostrikova[2], Anna S. Sergeyeva[1], Valeriia V. Studenok[1]

[1]UNIIM – Affiliated Branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
Researcher ID: G-6171-2017, e-mail: lab241@uniim.ru

[2] V.M. Gorbatov Federal Research Center of Nutrition Systems of Russian Academy of Sciences, Moscow, Russia

Keywords: nutrition products, reference materials, measurement standards, primary reference measurement procedure, lyophilization, freeze-drying, nutritional values

According to ISO Guide 35 [1] water is the main interfering impurity in the development of reference materials (RM). High concentration of the water causes an increase in the inhomogeneity of the RM and reduces its period of validity. That's why it is necessary to minimize water concentration when development of the RM takes place. It's especially relevant when developing RMs for composition of nutrition products whereas mass fraction of water in the starting materials can reach 80 % or more. In this connection, there is importance not only to remove excess water but also to maintain the structural integrity of the product, its protein composition, content of micro-and macroelements. Among the various methods of drying used in nutrition industry, the lyophilization (syn. freeze-drying) is one of the most popular and rapidly advancing technological processes. Lyophilization is the method of substances drying which includes deep freeze (from -30°C to -105°C) of substance of liquid or solid state before it dry and then it is placed in a chamber in which, under the influence of vacuum and low temperature, the frozen solvent is removed (sublimated), i.e. the solvent passes into the gaseous state from the solid, bypassing the liquid. This makes it possible to obtain dry tissues, preparations, products, etc. without losing their structural integrity and biological activity [2]. The advantages of the lyophilization are: preservation of the most important native properties (food and biological values); high homogeneity; long shelf life of the dried product. This method is suitable for drying thermally stable and oxidizing phytogenous/zoogenous substances and materials due to either a combination of vacuum drying and low temperatures, or a complete lack of heating.

The lyophilization is wide-used for production of foreign RM for composition of food raw material and nutrition products. At the same time, the two main tasks are being solved [3]. First of all, improved stability and extended shelf life of RM, e.g. when producing the RMs for composition of juice [4] or meat products [5]. Secondly, usage of lyophilization enables to add extra components in the composition of the RM during the process of its preparation such as vitamins, heavy metals, mycotoxins, polycyclic aromatic hydrocarbons (PAHs), pesticides, antibiotics, etc. [6]. In connection with these issues, the development of lyophilization in production of homogeneous and stable RMs for nutrition is relevant. This research is related to usage of lyophilization system during the preparation process of the RMs for composition of nutritive products based on example of RM for composition of chicken meat.

Poultry meat was used as the source material: white meat (chicken breast, sample 1) and red meat (chicken thigh, sample 2). For lyophilization, a freezer LCexv 4010-23B-001 manufactured by Liebherr (Austria) and a freeze dryer Scientz-10ND manufactured by Scientz (China) were used. The dryer has 3 sections for drying (1 – upper, 2 – middle, 3 – lower) on the different distance from the main device which drying conditions may vary. A thermocouple is placed in the tray with the test material, which allows you to track its temperature. Measurement of the mass fraction of water was performed using standard installation of air-heat drying from composition of State primary standard of units of mass fraction and mass (molar) concentration of water in solid and liquid substances GET

173-2017. Measurement of the mass fraction of nitrogen (protein) was performed by Kjeldahl method on the base of State primary standard of units of mass fraction and mass (molar) concentration of components in solid and liquid substances and materials based on volumetrical titration method of analysis GVET 176-1-2010. Measurement of fat mass fraction was performed according to State primary reference measurement procedure (PRMI) of fat mass fraction in nutrition products and food staples (FR.PR1.31.2019.00001).

Before the lyophilization procedure performed, the samples were boiled for 1 hour, released from the bones, cut into pieces with the size of the sides no more than 5 mm. Fragmented meat was distributed in a thin layer in three trays from the complex of Scientz-10ND dryer and placed to freezer LCexv 4010-23B-001 with prepared temperature of -25 °C. The got material was weighted on each stage. The process of lyophilization was performed with some stages. After the first stage, the material was chopped by laboratory mill. On each stage, the temperature of the material was recorded. Owing to special feature of the analysis is the placement of the cooled sample (from the freezer) on the trays of the freeze-dryer Scientz-10ND complex placed in conditions of indoor temperature, the temperature sensor is taken place in the layer of the sample, placed directly on the surface of the tray (at the frontier of sample and the tray in beginning of the experiment is the max temperature gradient; during the experiment temperatures become equal). Hereinafter, this temperature identifies sample temperature. The variation of temperature on the each stage of lyophilization of sample №2 (chicken thigh) is presented on the Figure 1.

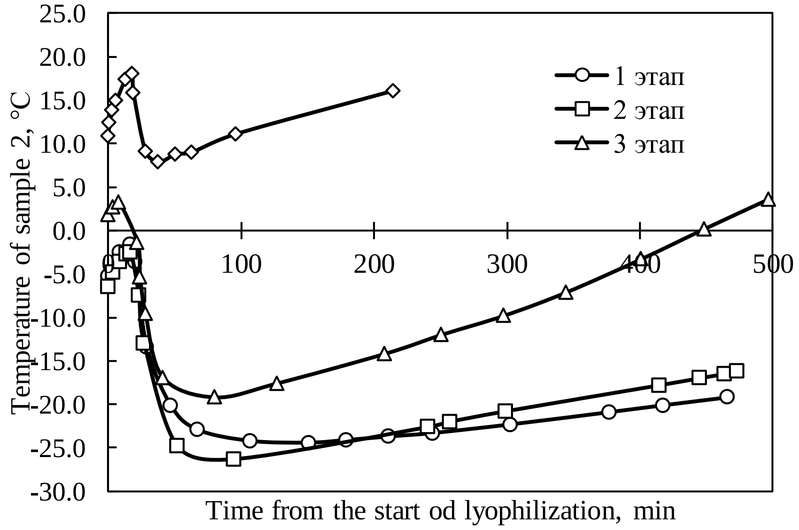

Fig. 1. Sample 2 temperature variation (chicken thigh)

The time of sample reaching the temperature near 20 °C is taken as the end of lyophilization process. Further increase in temperature will lead to destruction of the material and release of other than water components. Total time of lyophilization for samples №1 and №2 is 19 and 28 hours, respectively. Total mass loss for sample №1 is 68%, for sample №2 is 65%.

Then we performed estimation, using GET 173, by value of moisture mass fraction of homogeneity of material which was dried on the different trays, selected in 4 charges and dried on each of 3 trays. Processing of the results was performed following to Ivanov et al algorithms [7]. With usage of F-test we got the difference of mass fracture of moisture value of materials dried on different trays is statistically significant, i.e. the material is non-homogeneous. In this connection, we performed additional procedure of homogenisation that includes chopping by laboratory mill, intense stirring and conditioning. After got lyophilized and homogenized material, the measurement for mass fraction of moisture, nitrogen (protein) and fat were performed. The results of the measurements are presented in the table №1.

Table 1. Results of measurement for mass fraction of moisture, nitrogen (protein) and fat of boiled and freeze-dried poultry meat

Quantity	**Value**	
	Sample 1	**Sample 2**
Mass fracture of moisture, %	4,48	6,25
Mass fraction of nitrogen*, %	14,74	12,21
Mass fraction of protein*, %	92,12	76,34
Mass fraction of fat*, %	7,9	23,8
* — equivalent to absolutely dry substance		

Non-homogeneity and stability of got material are researched in the framework of experiment in purpose of certifying the type by algorithms stated in ISO Guide 35 [1]. Reference Material for composition of the boiled and freeze-dried poultry meat is entered in the register of certified types under the number GSO 11276-2019. The usage of lyophilization allowed providing the shelf life equal to 6 months at an ambient temperature (7 ± 3) °C and a relative humidity of no more than 60 %.

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ENSURING INTEGRITY AND RELIABILITY OF MASS MEASUREMENTS WITH CUBIS 2 BALANCES

Viktor S. Milokumov, Elena E. Arbenina

LLC "Sartorius RUS", Saint Petersburg, Russia
e-mail: anna.isakova@sartorius.com

Keywords: balances, mass measurements, reliability, measurement results, task management, data identification, data transfer, measurement protocol

Provision of information security is currently one of the most urgent tasks of the entire country in general and of each enterprise in particular. The upward trend of digitalization of industry and economy can significantly increase labor productivity, but at the same time, it creates new challenges in ensuring the protection and reliability of data.

This largely applies to the work of analytical and research laboratories, including mass measurements performed in laboratories. Sartorius, as one of the world's leading manufacturers of weighing equipment, is dedicated to meeting current and future user needs as much as possible. For this reason, Cubis 2 balance series, introduced in 2019, is equipped with a number of features to ensure the safety and reliability of measurements.

The term "reliability" does not have an unambiguous interpretation, and in this work, it is used in the meaning of "the correctness of the measurement result, the absence of errors, provided by technical means and documented."

The purpose of this work is to identify the main threats to safety and reliability of the results of laboratory mass measurements and the capability of Cubis 2 balances to eliminate them.

Based on the results of the analysis, a number of factors were identified that affect the reliability of the measurement results. These factors were classified, depending on the source of their occurrence, into 4 groups:

- associated with the data source, these include the identification of the operator, the device, the time of the measurements and the object of the measurements.
- related to the correctness of the measurement procedure, including: timely adjustment of sensitivity, horizontal installation, central location of the load, vibration exposure, exposure to static electricity, correct performance of the measurement procedure;
- associated with the fixation and transmission of data, in particular: fixation time, human factor in fixing data, loss and distortion of data during transmission;
- related to the storage and reproduction of data, namely: limitations on the duration and volume of data storage, as well as data loss as a result of technical failures or user actions and the correct reproduction of stored data.

The next stage of the work was to evaluate the technical solutions implemented in Cubis 2 series of laboratory balances from Sartorius, in terms of their sufficiency to ensure the reliability of the measurement results, taking into account the influence of the above factors.

As a result, the following was established.

The user management system implemented in Cubis 2 balances allows you to create accounts for each operator, set access levels for each operator or a group, and the Electronic Signature application allows you to uniquely identify the operator who performed certain measurements. The Audit Trail application records all user actions in non-volatile memory.

The "ISO / GLP protocol" function includes in each measurement protocol data about the measuring device, date and time of measurement.

Barcode printing application (with QR code support) allows you to codify measurement results or other data, such as sample ID, to automate their accounting during storage, movement and use in the laboratory, thus increasing productivity and reducing risk errors.

The task management function allows you to create measurement tasks based on built-in applications, including presetting up to 6 IDs for each sample and batch of samples.

The isoCAL automatic internal calibration and sensitivity adjustment system continuously monitors the temperature of the weighing cell and, if necessary, performs calibration and adjustment in automatic mode. Likewise, the Q-level system controls the horizontal position of the installation.

The Q-Pan system measures the torque due to the off-center load position and compensates for the resulting error.

4-level vibration and response time filters, as well as stabilization time and range settings, compensate for vibration effects and provide accurate measurements in unstable conditions.

The ionizer built into the “I” model draft shiled can be set to automatically start, eliminating the possibility of static electric charge affecting the measurement results.

The software of the balance, which works on the principle of individual measuring tasks based on pre-installed applications, allows you to pre-set the measuring process. As a result, the operator receives step-by-step instructions on how to perform the task, thereby minimizing the risk of making an error during the measurement process.

Based on the results of the measurement, a protocol is formed, which is then saved to media (paper or electronic) in accordance with the selected printing profiles. Non-editable PDF format is supported. Each saved log file is accompanied by an MD5 checksum calculation. When transferring data over the local network, the encrypted data transfer protocol HTTPS is used. Thus, changing the data in the process of recording and transferring is impossible.

The "Alibi-memory" function automatically saves all measurement results in the internal non-volatile memory of the balance, completely protected from both intentional changes and errors due to technical failures, for example, in case of a sudden power outage.

Based on the foregoing, the following conclusion was made: the complex of technical solutions implemented in the Cubis 2 balance series from Sartorius makes it possible to guarantee the error-free receipt, recording, identification, transmission and storage of measurement results, thereby ensuring their reliability.

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ABOUT THE METROLOGICAL ASSURANCE OF THE GAS CALORIMETERS AND WOBBE INDEX ANALYZERS

Karina A. Mishina, Elena N. Korchagina, Yaroslav V. Kazartcev, Anna V. Kolobova

D.I. Mendeleyev Institute for Metrology, Saint Petersburg, Russia
e-mail: E.N.Korchagina@vniim.ru

Key words: calorific value, Wobbe index, gas calorimetry, gas chromatography

Due to the raising awareness about ecology problems, the issue of effective use of energy sources is getting increased attention around the world. The industry is committing to a fuller use of conventional energy sources both with the byproducts of their production and processing, such as coke oven and blast furnace gas, associated petroleum gas, coal bed methane and others. Lately the use of gas fuels has been raising in average by 1,8 % per year and is prognosed to increase even more, mostly in the cities and countries with strict ecological regulations [1]. Compared to other fuels natural gas has an important advantage combining high heating intensity and efficiency with low emissions of carbon and nitrogen oxides and virtually no pollution by ash particles and sulphur.

An extensive research in the field of renewable energy results in numerous processes that allow to derive low- and high-calorie gas products, including biogas, from waste of agricultural, paper and other industries. The conducted analysis shows that, in comparison to the natural gas, these gas fuels differ substantially in their calorific value and composition. Moreover, the fact that the composition and quality of such gas mixtures can change substantially both in the long- and short-term requires special attention to the interchangeability of the fuels in order to maintain efficiency and avoid an increase of the emissions and damage to the equipment used for energy recovery.

The main interchangeability characteristic – Wobbe index – reflects information about a thermal load for the system since gases with different compositions and calorific values but the same Wobbe indices have the same thermal power and can be used with the same nozzle.

Wobbe index (superior W_{sup} or inferior W_{inf}) can be calculated from the calorific value (superior H_{sup} or inferior H_{inf}) and relative density d using the formula:

$$W_{sup/inf} = \frac{H_{sup/inf}}{\sqrt{d}} \qquad (1)$$

The inferior calorific value H_{inf} can be calculated from the gas composition according to ISO 6976 or determined by calorimetric measurement methods described in ISO 15971. Calorimetric methods, in comparison with commonly used ISO 6976 – a method for calculation of calorific value and other properties from gas composition, usually determined by a chromatograph – have several advantages in application in some cases, especially for non-conventional gases: absence of limits for the content of components such as hydrogen and ethane, lower uncertainty and response time, and more cost-effective and easier maintenance and calibration [2].

There are several types of measurement equipment for determination of calorific value and Wobbe index based on calorimetric measurement methods, which are currently used in industry. International standards ISO 15971 and OIML R 140 describe classification and normative requirements for the accuracy of such instruments (Tables 1 and 2).

Table 1. Maximum permissible errors according to ISO 15971 [3]

Class	**0**	**1**	**2**	**3**
H_{sup}	± 0,1 %	± 0,1 MJ/m^3 (~ 0,25 %)	± 0,2 MJ/m^3 (~ 0,5 %)	± 0,5 MJ/m^3 (~ 1 %)

Table 2. Maximum permissible errors according to OIML R 140 [4]

Accuracy class	**A**	**B**	**C**
Energy	± 1,0 %	± 2,0 %	± 3,0 %
H_{sup}	± 0,5 %	± 1,0 %	± 1,0 %

The quality of the results obtained with these measuring instruments usually heavily depends on calibration, but options for it are quite limited. ISO 15971 only suggests pure methane, gas mixes with a calculated calorific value, and gases, certified using a reference calorimeter. The first two options are not optimal for measurement equipment working outside of the natural gas range. The third option is preferable as it also provides direct traceability to the unit of the energy of combustion.

Currently the metrological assurance for such instruments is provided using the calibration standards developed at VNIIM and used for type approval, calibration and verification. These tools are not always sufficient for the consumer's demand for easily available materials with a certified calorific value to be used for quality control and routine calibration. To meet this demand, VNIIM Research Laboratory of Combustion Calorimetry in cooperation with Research Laboratory of Gas Analysis started the development of a set of certified reference materials of the inferior volumetric calorific value based on the transfer standards of pure gases which molar composition is certified and traceable to GET 154 – State Primary Measurement Standard of units of molar fraction, mass fraction, and mass concentration of components in gas and gas-condensate medium. In order to determine target calorific values and their uncertainty for the CRM development, the characteristics of commonly used field instruments, that have been confirmed through type approval procedure, were considered and are given in Table 3.

Table 3. Overview of instruments for calorific value and Wobbe index measurement

Instrument	**Measurement quantity**	**Measurement range**	**Uncertainty, %**
9610, Cosa Xentaur Corporation	$W_{inf/sup}$, $H_{inf/sup}$	1 – 95 MJ/m^3	± 1,0
	d	0,1 – 3,0	± 0,6
NKS, OOO Teplofizichiskie pribory	H_{inf}	25 – 41 MJ/m^3	± 0,3
RBM 2000, Reineke Mes-und Regeltechnik GmbH	$W_{inf/sup}$, $H_{inf/sup}$	3 – 100 MJ/m^3	± 1,0
		28 – 40 MJ/m^3	± 0,6
	density, ρ	0 – 2 kg/m^3	± 1,0
Gas-lab Q1, Elster GmbH	$H_{inf/sup}$	30,4 – 47,2 MJ/m^3	± 0,4 (± 0,2*)
	density, ρ	0,71 – 0,97 kg/m^3	± 0,8 (± 0,4*)
CWD 2000, UNION Instruments GmbH	H_{inf}	2,5 – 50,0 MJ/m^3	± 1,0
	W_{inf}	2,5 – 55,5 MJ/m^3	± 1,0
CWD 2005, UNION Instruments GmbH	$H_{inf/sup}$	3,0 – 5,0 МДж/м^3	± 1,0
		12,5 – 21,0 МДж/м^3	
WI, Reineke Mes-und Regeltechnik GmbH	H_{inf}	2,5 – 55,5 MJ/m^3	± 1,5
	W_{inf}	2,5 – 56,0 MJ/m^3	± 1,0
KSNG-05, OOO Teplofizichiskie pribory	H_{inf}	25 – 50 MJ/m^3	± 0,5
		31,8 – 39,8 MJ/m^3	± 0,45
EMC 500, RMG Messtechnik GmbH	$H_{inf/sup}$	30,2 – 47,2 MJ/m^3	± 0,5
	density, ρ	0,65 – 1,3 kg/m^3	± 0,5
66, Reineke Mes-und Regeltechnik GmbH	H_{sup}	32 – 42 MJ/m^3	± 0,5
WIM 9900, Horbe Instruments B.V.	W_{inf}	40 – 60 MJ/m^3	± 2,0
	d	0 – 2	± 0,2
WIM Compas	$W_{inf/sup}$	0 – 90 MJ/m^3	± 1,0
	$H_{inf/sup}$		± 0,7
	d	0,5 – 1,7	± 1,0
*with special calibration			

Based on the conducted research, technical characteristics for the starting material and metrological characteristics for the developed CRM were established and are given in Tables 4 and 5.

Table 4 – Technical characteristics of the starting material

CRM index	Starting material		
	Main analyte	**GSO number**	**Range of permissible values of the main analyte, mole fraction, %**
NOTS-VNIIM-H2	Hydrogen (H_2)	GSO 10768-2016	от 99,95 до 99,9995
NOTS-VNIIM-CH4	Methane (CH_4)		от 99,95 до 99,999
NOTS-VNIIM-C2H6	Ethane (C_2H_6)		от 99,90 до 99,999
NOTS-VNIIM-C3H8	Propane (C_3H_8)		от 99,80 до 99,999

Table 5.Certified characteristic, range of permissible certified values and permissible value of expanded uncertainty for the developed CRM NOTS-VNIIM

CRM index	**Range of permissible certified values of the inferior volumetric calorific value, $H_{inf}^{25/20}$, MJ/m^3***	**Permissible value of the relative expanded uncertainty (U)** with coverage factor k = 2, %**
NOTS-VNIIM-H2	10,030 – 10,260	0,3
NOTS-VNIIM-CH4	33,350 – 33,580	
NOTS-VNIIM-C2H6	59,740 – 59,980	
NOTS-VNIIM-C3H8	86,230 – 86,470	

Notes:

* – upper index reflects the reference conditions at which the certified calorific value is determined – combustion reference conditions : temperature 25 °C (298,15 K) and pressure 101,325 kPa, and metering reference conditions at which the volume of fuel to burn is notionally determined: temperature 20 °C (293,15 K) and pressure 101,325 kPa.

**– corresponds to relative error with confidence probability (P=0,95).

Two new calorimeters USVG and USNG with a measurement range from 3 to 90 MJ/m^3 and expanded uncertainty up to 0,4 % were developed in 2017 as part of GET 16 – State Primary Standard of the Unit of Energy of Combustion, Specific Energy of Combustion and Volumetric Energy of combustion and are currently being used for the determination of the certified calorific value. The purity of the starting material and its homogeneity and stability is thoroughly controlled using the GET 154 equipment in accordance with the same procedures that are applied for the production of the transfer standards. Relative density and, consequently, Wobbe index, for each pure gas can be calculated using the equations of state provided in GSSSD standards.

At this moment the development stage for the described set of CRMs have been completed. The type approval is planned to be finished by the end of 2020.

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DEVELOPMENT NEW TYPES OF CERTIFIED REFERENCE MATERIALS WITH THERMODYNAMIC PROPERTIES FOR METROLOGICAL SUPPORT OF MEASUREMENTS IN THE FIELD OF THERMAL ANALYSIS AND CALORIMETRY IN THE RUSSIAN FEDERATION

Andrey M. Nepomiluev, Vyacheslav V. Kazantsev, Artem P. Shipitsyn

UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
e-mail: kazantsev@uniim.ru

Keywords: reference materials, thermal analysis, specific enthalpy, specific heat, phase transition heat

Certified reference materials (CRMs) of thermophysical properties are a traditional means of ensuring the uniformity of measurements in various types of thermal analysis. One of the main parameters measured in the thermal analysis of various substances are the temperature and phase transition heat (enthalpy) and the specific enthalpy. Calibration and verification of temperature and enthalpy measuring instruments are carried out using reference materials (RMs) of temperature and fusion heat. In this case, it is necessary to have different types of RMs based on different materials in temperature and phase transition enthalpy. The recognized world leader in the production of thermoanalytical equipment Netzsch Geratebau GmbH (Germany) offers its users 24 items of various materials for manufactured measuring instrument calibration and graduation, which cover almost the entire range of temperature and specific enthalpy. It includes both metals and non-metals - 12 items of each type.

There were developed 9 types of geophysical properties on corundum, potassium chloride, stainless steel, gallium, indium, tin, zinc, antimony and molybdenum basis in UNIIM. A comparison of the characteristics of manufactured CRMs with foreign RMs [1,2] shows that the certified CRM characteristics are consistent with the declared measurement uncertainties. Technology for the production of RMs has been developed that meets the requirements of customers in terms of the shape and weight of RMs and ensures the uniformity and stability of the certified characteristics.

Currently, UNIIM - Affiliated Branch of the D.I.Mendeleyev Institute for Metrology is working on the development of temperature and phase transition enthalpy CRMs based on bismuth, aluminum, silver, gold, as well as CsCl, Ag_2SO_4, $BaCO_3$, which will allow continuing further improvement of the system for transferring units from primary standards to measuring instruments during testing, verification, calibration of measuring instruments, certification of measurement techniques (methods).

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REQUIREMENTS FOR REFERENCE MATERIALS IN ACCORDANCE WITH ISO / IEC 17025

Narine G. Oganyan

All-Russian Scientific Research Institute of Physical Technical and Radio Technical Measurements
Moscow region, Mendeleevo, Russia
e-mail: oganyan@vniiftri.ru

A wide range of human socio-economic activities are based on measurements in the field of chemistry and biology. Thousands of such measurements are carried out every day, the accuracy and reliability of which influence on the decisions about the food safety, the health of people and animals, the environmental protection, etc. They are important not only for domestic policy of a country, but also for the world market in the process of minimizing technical barriers to trade. Therefore, the concept of “tested once, accepted everywhere” is becoming more and more important. Today, the results of the measurements compared across space and time have been considered the best. The accuracy and reliability of these measurements depends critically on the competence of the staff carrying out the measurements, on the chosen methods / procedures of measurements, on the traceability of the used measuring instruments and reference materials to the corresponding primary standards of units. The general requirements for the competence of testing and calibration laboratories, regardless of the field of measurement, are described in the international standard ISO / IEC 17025 [1]. However, measurements in the field of chemistry and biology have their own specifics and differ sharply from traditional physical measurements. In order to adapt the technical requirements of the standard for the field of chemistry and biology, Recommendation series have been developed and continue to be developed by International organizations specializing in these fields for the unambiguous interpretation of the requirements both by the personnel of measuring laboratories and by technical experts assessing the competence of these laboratories in accordance with ISO / IEC 17025 requirements all over the world.

In this paper the requirements of ISO / IEC 17025 for reference materials is detailed coverage based on analysis of Recommendations developed by such organizations as: International Laboratory Accreditation Organization (ILAC); International Traceability Cooperation in Analytical Chemistry (CITAC); International Union of Pure and Applied Chemistry (IUPAC); Center for Analytical Chemistry in Europe (EURACHEM) [2-7].

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IMPROVEMENT OF METROLOGICAL SUPPORT OF METHODS AND MEANS FOR DETERMINING pH VALUE IN AQUEOUS SOLUTIONS

Sergey V. Prokunin, Andrei. N. Shchipunov, Vladimir I. Dobrovolskiy

All-Russian Scientific Research Institute of Physical Technical and Radio Technical Measurements
Moscow region, Mendeleevo, Russia
e-mail:prokunin@vniiftri.ru

Keywords: pH, primary standard, comparisons, buffer solution, pH value, fixanals

State primary pH standard (GET 54) forms the basis of the system of metrological support for electrochemical measurements, from which the pH values are transmitted to the working pH standards of 1, 2, 3rd categories and measuring instruments (pH meters and measuring electrodes). The pH values are reproduced by reference solutions, the parameters of which are controlled by reference measuring installations according to the methods corresponding to the recommendations of the OIML [1] and IUPAC [2].

In 2019 the Federal State Unitary Enterprise "VNIIFTRI" carried out the improvement of the State primary standard of the pH ion activity value in aqueous solutions with the assignment of registration number GET 54-2019 to it. The improvement of the system of metrological support in the field of pH-metry was carried out taking into account the overall development of science and technology, as well as the main industries.

The improvement of the standard is due to the necessity to develop a method and means of reproducing, storing and transmitting the pH value in the strongly acidic pH range from 0 to 1.0, for metrological support of measuring instruments, including medical equipment for clinical diagnostics of the human gastrointestinal tract.

The improved State primary standard of the pH value of the hydrogen ions activity in aqueous solutions is designed to reproduce, store and transfer the pH value of the hydrogen ions activity in aqueous solutions in the range of values from 0.01 to 12.

The set goals were achieved by introducing six new measures of acidity with pH values equal to 0.01 into the standard; 0.10; 0.260; 0.528; 1.00 and 1.20, respectively. The measures were prepared from purified hydrochloric acid with the addition of ultrapure potassium chloride. The molar concentration of acidity measures ranged from 1.0 to 0.1 mol / kg, which was confirmed by control measurements on a high-precision coulometric installation.

The state primary standard ensures the reproduction of the pH value of the activity of hydrogen ions in the strongly acidic area with the root-mean-square deviation of the measurement result not exceeding 0.0015 at a temperature of 25 ° C with 10 independent measurements, in the range of pH values from 0.01 to 1.0. The residual systematic error does not exceed 0.02 at a temperature of 25 ° C, in the range of pH values from 0.01 to 1.0.

Сравнение характеристик эталонов с зарубежными аналогами приведено в таблице 1.

The standard uncertainty of measuring the pH value of the activity of hydrogen ions in aqueous solutions, in the range of pH values from 0.01 to 1.0, estimated by type A is 0.0015, estimated by type B is 0.0083. The total standard uncertainty is 0.0084. Expanded uncertainty is 0.0168 with a coverage factor of k = 2.

Comparison of the standard performance with foreign analogues is shown in Table 1.

Based on the data given in Table 1, it is certain that the State Primary pH Standard GET 54-2019 corresponds to the best world analogues.

The final stage of the work was the revision of the state verification scheme for pH measuring instruments, which is the basis for creating a system for ensuring the uniformity of measurements in the field of pH-metry both in Russia and in the CIS countries. The scheme takes into account the state and the near-term development prospects of pH-metry in Russia. It is drawn up in such a way that for each measuring device the order and method of subordination in the unified state verification system is established.

Table 1. Comparison of pH standards of foreign national metrological institutes

	GET 54-2011	GET 54 -2019	NIST (USA)	NMIJ (Japan)	NIMT (Thailand)
pH range	1 - 12	**0.01** - 12	1.2 - 12	1.18 - 12	1.00 - 12
Expanded uncertainty (k=2, P=0.95)	0.0024	0.0024 – pH 1 – 12 0.0168 – pH 0.01 – 1,00	0.001	0.003	0.02

The necessity to revise the verification scheme is associated with the arising need for metrological support for a new line of pH measuring instruments, which are distinguished primarily by high accuracy in many branches of science and industry: in clinical laboratory diagnostics, microbiology, production of medicines, food products, cosmetics, etc.

Conclusions:

1. The State primary standard for the pH value of the activity of hydrogen ions in aqueous solutions GET 54 has been improved.
2. The metrological characteristics of the improved standard GET 54 meet the requirements for metrological characteristics necessary for the verification of the entire line of pH measuring instruments used in the territory of the Russian Federation.
3. Improvement of GET 54 made it possible to ensure the uniformity of pH value measurements in the strongly acidic area of the pH range from 0.01 to 1.0.
4. 6 new values of acidity measures have been introduced (0.01; 0.1; 0.260; 0.528; 1.00; 1.20).
5. The improved GET 54 corresponds to the best world analogues.

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RECENT DEVELOPMENTS IN THE CERTIFICATION OF ORGANIC REFERENCE MATERIALS BY ^{1}H, ^{31}P AND ^{19}F QUANTITATIVE NUCLEAR MAGNETIC RESONANCE (QNMR)

Alex Rueck, Christine Hellriegel, Kathrin Breitruck, Markus Obkircher

Merck KGaA /Sigma-Aldrich Production GmbH, 9471 Buchs, Switzerland
e-mail: Kathrin.breitruck@merckgroup.com

Over the last decades quantitative NMR (qNMR) spectroscopy has become an important tool for the content determination of organic substances and the quantitative evaluation of impurities. Since the signal intensity is directly proportional to the number of protons contributing to the resonance, qNMR is considered as a relative primary method [1-3]. Quantitative NMR in combination with metrological weighing was optimized to show the power of the measurement method [4]. The implementation of qNMR in new fields of application (e.g. metabolomics, biomarker discovery, physiological pathways) brings along complex molecules and systems, thus making the usage of 1H-qNMR more challenging. The use of other NMR active nuclei provides an elegant solution for which new qNMR standards are required. Therefore, we developed two additional classes of qNMR Certified Reference Materials (CRM) based on different NMR active nuclei, namely 31P and 19F [5,6]. Traceability to the SI was achieved using primary Reference Materials from the National Institute of Standards and Technology (NIST) [7] and the National Metrology Institute of Japan (NMIJ). In addition to the neat material CRM, we also present the development of new CRM for qNMR, which are ready-to-use in deuterated solvents.

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DNA REFERENCE MATERIALS FOR PROVISION OF NUCLEIC ACID MEASUREMENT RESULTS METROLOGICAL TRACEABILITY

Andrei L. Runov, Elena V. Kurchakova, Maxim S. Vonsky

D.I.Mendeleyev Institute for Metrology, Saint Petersburg, Russia
ORCID: 0000-0001-9496-4414, e-mail: a.l.runov@vniim.ru

Keywords: reference material; DNA; real-time polymerase chain reaction; real-time PCR

DNA measurements are broadly included in the practice of clinical laboratory diagnostics, veterinary medicine, sanitary control and testing for GMO in food and feed. Thousands of PCR analyzers operate in analytical laboratories of the Russian Federation to carry out these measurements, a significant amount of them subject to the state regulation of ensuring the uniformity of measurements and require verification.

Nucleic acids analysis implies both the study of a nominal property - the sequence of nucleotides forming the DNA/RNA chain, and absolute or relative measurement of the quantitative content of specific fragments of nucleic acids. Determining the sequence of nucleotides is the field of sequencing. This method assumes the presence of reading errors, the frequency and probability of which can be quantified. World practice implies the use of reference materials of genomic DNA, characterized by nucleotide sequence, to determine the accuracy of existing sequencers.

Quantitative determination of specific DNA fragments content is almost always performed using methods based on the polymerase chain reaction (PCR). In the overwhelming majority of practical applications, real-time PCR is used, a method that allows one to quantify relative content of a specific DNA fragment in a sample.

Since real-time PCR is a relative method, its applications for the quantitative determination of DNA targets requires the use of reference materials. Typically, such reference materials appear to be calibrators provided by the manufacturer of test systems, which do not have any formal status, and the quantitative characteristics assigned to them do not ensure metrological traceability to the national standard or CRMs. This leads to the fact that the results of measurements performed in different laboratories using different test systems may not be comparable with each other.

A wide range of analytical problems solving by DNA measurement applications requires the creation of a large amount of reference materials, characterized both by the nucleotide sequence and by the quantitative content of specific DNA fragments.

The only DNA certified reference material currently produced in the Russian Federation is CRM 9866-2011 – reference material of soybean DNA, developed by VNIIM in 2011. Reference material is certified for the mass fraction of genetically modified soybean DNA (event 40-3-2) in natural soybean DNA and consists of three vials containing soybean DNA solutions with a mass fraction of GM soybeans 50 g/kg, 10 g/kg and 1 g/kg, respectively. This reference material is mainly used for verification of real-time PCR analyzers, although it can be used for quantitative analysis for the GMO presence in soybeans (event GTS 40-3-2) for in-laboratory quality control and to ensure traceability to the national measurement standard GET 208-2018. Application CRM 9866-2011 makes it possible to classify real-time PCR analyzers as measuring instruments, but this is not enough: the widespread use of the real-time PCR method requires certification of reference materials for quantitative analysis of various DNA targets. At the same time, the variety of analyzing biological objects requires creation of a large number of certified reference materials for providing metrological traceability of routine DNA measurements results.

Currently, digital PCR (dPCR) is considered as a candidate reference method for measuring the quantitative content of specific DNA fragments. Digital PCR is used for certification of DNA CRMs by the world's leading metrological institutes. Applying of droplet-digital PCR method allowed VNIIM to participate successfully in the international key comparisons of the CCQM BIPM working group on nucleic acid analysis K86.c and confirm the measurement capabilities (CMC) of the Russian Federation in the field of nucleic acid analysis. This allows the development of reference DNA materials, and confirm their recognition at the international level.

Nowdays, NIST (USA), NIBSC (UK), JRC (EU) and NIM (China) are the leaders in the production of CRMs of DNA certified by copy number. In the Russian Federation, there are no CRMs, certified by copy number of specific DNA fragments. VNIIM is developing a new CRM based on human DNA - the HeLa-VNIIM CRM with certified characteristics of the specific DNA fragments copies number in the human genome, as well as the ratio of the number of copies of specific DNA fragments. Reference material is produced as a solution of DNA isolated from HeLa S3 cells in TE buffer (10 mM Tris, 1 mM EDTA, pH 8). Cells of HeLa S3 tissue culture contain human papillomavirus type 18 integrated in human genome. The genome of HeLa cells has been characterized, this cell line is stable and is stored in most cell collections in the world. The isolated and purified DNA of HeLa cells can be certified for the copy number of specific DNA fragments by dPCR. The presence of an HPV-18 DNA fragment in the genome makes it possible to use the developed CRM for quality control of HPV-18laboratory diagnostics.

We have shown that the quantity of specific fragments for the selected set of genes corresponds to their content in the human genome, which makes it possible to use the developed CRM as an analogue of the NIST 2372a reference material. SRM NIST 2372a is a solution of human genomic DNA isolated from donor peripheral blood cells. It is characterized by the copy number of human DNA (copies per μl). This characteristic is averaged over the content of ten specific DNA fragments.

The CRM under development will be certified by the total DNA content (similar to SRM 2372a NIST), by the ratio of two DNA fragments copy number (similar to CRM 9866-2011) and by the copy number concentration of each individual specific DNA fragment (there are no analogues). The availability of CMC in the field of DNA measurements and comparison with the NIST 2372a reference material provides the necessary level of metrological traceability of the developed CRM. A reference material of the composition of specific DNA fragments in the matrix of human genomic DNA characterized by copy number concentration can be applied not only for verification and calibration of DNA analyzers, but also for standardization of measurements in forensic and clinical diagnostic laboratories.

ACTUAL PROBLEMS IN CELL ANALYSIS REFERENCE MATERIALS DEVELOPMENT

Andrei L. Runov[1], Natalya N. Shevchenko[2], Tatyana S. Goryachaya[1,3],
Elena V. Kurchakova[1], Maxim S. Vonsky[1]

[1]D.I.Mendeleyev Institute for Metrology, Saint Petersburg, Russia
[2]Institute of Macromolecular Compounds of the Russian Academy of Sciences, Saint Petersburg, Russia
[3]Institute of Cytology of the Russian Academy of Sciences, Saint Petersburg, Russia
ORCID: 0000-0001-9496-4414, e-mail: a.L.runov@vniim.ru

Keywords: reference material, cell analysis, enumeration, synthetic RM

Cells quantification, as well as enumeration of cells characterized by certain features or certain physiological states, are the subject of cellular analysis, one of the recently identified areas of bioanalysis in metrology. This type of measurement is widely used in laboratory medicine; the development of cell technologies in the field of cell replacement therapy in regenerative medicine attracted special attention. A cell as an elementary unit of life is a complex multiparametric object, which can be described using simplified models, and quantitative measurements requiring the development of adequate reference materials.

The necessity of ensuring metrological traceability of measurement results in cell analysis encouraged BIPM in 2015 to separate the Working Group on Cell Analysis (CAWG) from the BIPM CCQM Working Group on Bioanalysis. The task of CAWG is to ensure the reliability and global comparability of cell measurements, including cells enumeration and determination of their functional properties in complex matrices and mixtures. To this end, CAWG have already carried a number of pilot comparisons, their participants have worked out technologies for the identification and counting of intact eukaryotic cells fixed on substrates (CCQM P123), cells expressing certain surface biomarkers (CCQM P102, P165).

Due to the complexity of cell as a living system interacting with changing environment, cell measurable parameters amount can be considerable. One of the CAWG primary goals is to determine the priority areas requiring the development of CRMs and reference methods in the first order. One of these areas of cell analysis is the enumeration of cells - a basic procedure, standardization of which is required to provide metrological support for more complex methods. This can be a simple recalculation of objects of the same type (used, for example, when determining the degree of contamination of drinking water with E. coli). To study the measuring capabilities of national metrological institutes (NMI) in this area, comparisons based on the material containing E.coli in water prepared by NIM of China are planned; P214 comparisons on cell quantification in suspension are underway. This area also includes the enumeration and selection of cells expressing certain surface factors - such measurements are used in cell therapy to select certain types of cells. The first round of pilot comparisons CCQM P165 on the count of CD34 + cells was carried out; pilot comparisons on differential counting of CD4 + and CD8 + cells are planned in the near future (number not assigned).

Cell counting can be performed both manually by the operator (using a microscope, in a Goryaev chamber or in a hemocytometer), or applying automatic systems (automatic hemocytometer or flow cytofluorimeter). At the same time, CRMs that can ensure the accuracy of cell counting are required for quality control. The question is raised about the comparability of the measurement results obtained by different methods.

Existing CRMs for cellular analysis are usually prepared from lyophilized living cells. Before use, such reference materials must be reconstituted with a special buffer and used immediately. The cells begin to die upon reconstitution, affecting certified characteristics of the reference material. CCQM P214 pilot comparisons of CAWG are currently underway, with the goal to determine the suitability of lyophilized peripheral blood cells as CRMs, to compare different cell counting methods and to study the components of the uncertainty budget for cell measurements.

There are also reference materials of certain types of cells that are stable over a relatively long period of time (up to 3 months). This, for example, is CRM 10669-2015 – reference material of blood cell composition, produced by VNIIM. It is a suspension consisting of leukocytes, erythrocytes and hemoglobin of animals in the plasma of donated blood. This CRM is stable for 3 months and can be used for verification and calibration of hematological analyzers in the field of health and veterinary medicine.

Nowadays CAWG is considering the use of synthetic reference materials to solve the instability problem of CRM based on lyophilized cells. VNIIM together with the Institute of Macromolecular Compounds of the Russian Academy of Sciences is currently developing a new reference material for cell analysis based on polymer materials. Reference material appears to be a set of synthetic objects corresponding in size and shape to the blood cells: toroids (erythrocytes), spheres (leukocytes) and elements of complex shape (platelets). We have developed a technology for the manufacture and differentiation of objects of a given shape with given size; this candidate reference material will be used in pilot comparisons of CAWG. The possibility of introducing fluorescent dyes into the composition of synthetic cell mimics to simulate expressed surface biomarkers has been shown. An incomplete analogue of the developed reference material in the world is the candidate CRM being developed at the NMIJ. It is a set of synthetic spheres of a given diameter and cannot be used to standardize the counting of cells with complex shapes. Our proposed synthetic reference material can be used as a starting point for the development of stable CRMs for cell measurements.

DEVELOPMENT OF COMPLEX FOR METROLOGICAL SUPPORT OF FOOD INDUSTRY

Anna S. Sergeeva [1], Natal'ia L. Vostrikova[2], Mary Yu. Medvedevskikh[1]

[1] UNIIM – Affiliated Branch of the D.I. Mendeleev Institute for Metrology, Ekaterinburg, Russia
ORCID: 0000-0001-8347-2633, e-mail: sergeevaas@uniim.ru

[2]Gorbatov Research Center for Food Systems, Moscow, Russia

Keywords**:** food products, certified reference material, measurement standard, primary reference measurement procedure, indicators of nutritional value, identification indicators

"Strategy to Enhance Food Quality in the Russian Federation until 2030" [1] was approved by Executive Order of the Russian Federation Government No. 1364-r on June 29, 2016 to reduce on the market proportion of products with low consumer properties, falsified products. In framework of implementation of this Strategy researchers of VNIIM-UNIIM are working on the creation of a metrological support complex for measurement instruments and procedures for measuring identification indicators and indicators of nutritional value of food products and food raw materials.

To date, the laboratory of metrology of moisture measurements and reference materials produces more than 40 types of certified reference materials (CRMs) of composition of food products, food raw materials and food additives which are necessary for metrological supporting measurement results of identification indicators of food products for compliance with the requirements of Customs Union Technical Regulation (Figure 1).

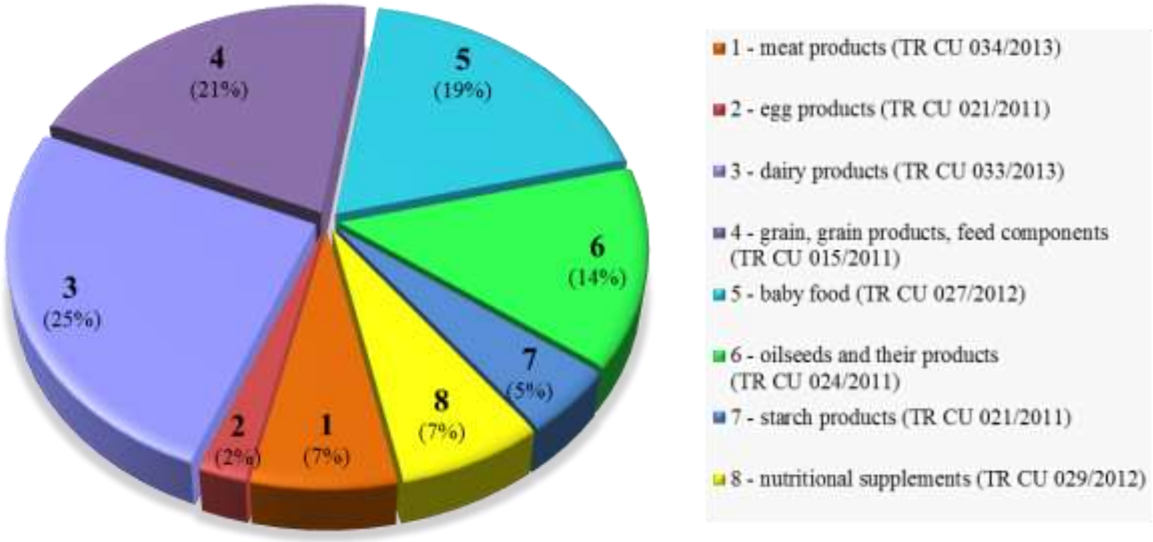

Fig. 1. Reference materials of food products composition

The certified characteristics of CRMs of food composition (content of moisture, fat, nitrogen (protein), ash, carbohydrates) are traceable to the State primary measurement standard of mass fraction and mass (molar) concentration of water in liquid and firm substances and materials GET 173-2017, the State secondary measurement standard of mass fraction and mass (molar) concentration of components in liquid and firm substances and materials by volumetric titration GVET 176-1-2010, primary reference measurement procedures for the determination of mass fraction of fat (FR.PR1.31.2019.00001), ash (FR.PR1.31.2019.00002), carbohydrates (FR.PR1.31.2019.00005), crude fat (FR.PR1.31.2019.00009) [2]. The certified characteristics of CRMs of food additives are traceable to the State secondary measurement standard of mass fraction and mass (molar) concentration of organic components in liquid and firm substances and materials by gas and liquid chromatography GVET 208-1-2016.

The development of CRMs is carried out in close cooperation with other organizations - specialists in the field of food industry. So, for example, the co-developer of GSO 11274-2019 / GSO 11276-2019 of freeze-dried meat products composition is Gorbatov Research Center for Food Systems, Moscow, GSO 11504-2020 / GSO 11505-2020 of dairy products composition - Ural State University of Economics, Ekaterinburg, GSO 11337-2019 composition of cystine - ZAO "LEKO CENTR-M", Moscow, GSO 11168-2018 of reconstituted milk composition - Xema Co. Ltd. [3, 4].

CRMs are actively used in testing for the purpose of type approval, verification and calibration of measurement instruments, interlaboratory comparison (ILC), metrological certification of measurement procedures and accuracy control of measurement results. Since 2019, more than 300 NMR analyzer and more than 80 IR analyzers have been verificated using CRMs of composition of oilseeds and products produced from these. CRMs of milk and dairy products composition and CRMs of meat products composition have been used for verification of more than 30 IR analyzers of food products and entry into the register of approved types of milk and dairy products analyzers (numbers in the State Register 78730-20, 79313-20).

The concept of developing CRMs in UNIIM is consistent with the international model of Food Composition Triangle, created by the Association of Analytical Communities AOAC [5]. This model (Figure 2) allows distributing all food products into nine sectors, depending on the content of protein, fat and carbohydrates. To validate the analytical method for most products located in one sector, it is sufficient to conduct studies on one or two food matrices from that sector.

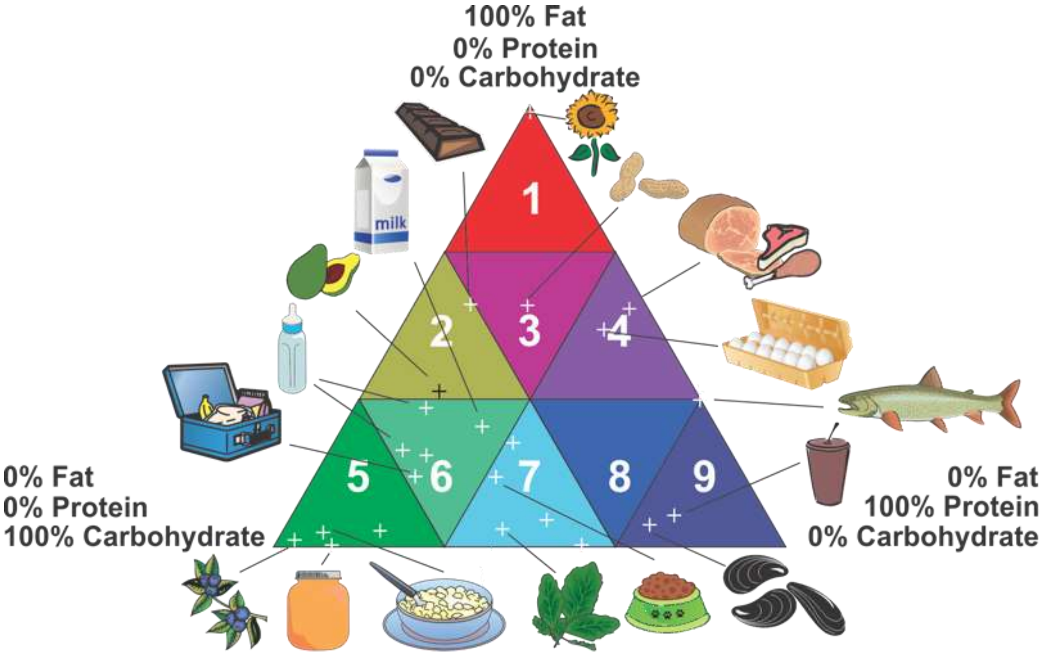

Fig. 2. AOAC Food Composition Triangle

In parallel with the development of the metrological support complex UNIIM is carrying out work on the recognition at the world level of measurement results of characteristics of food composition through participation in international proficiency testing programs, pilot and key comparisons. In 2020, as a result of successful participation in international key comparisons (CCQM-K149), the laboratory of metrology of moisture measurement and reference materials confirmed high accuracy of measurement results of nitrogen mass fraction in milk powder, grain, egg powder, cereals and feed and received new five lines of calibration and measurement capabilities (CMC) in database of Bureau international des poids et measures (BIPM).

Thus, the developed CRMs allow to ensure the uniformity of measurements for indicators of identification and nutritional value of food products and food raw materials durind establishing the compliance of products with the requirements of legislation on technical regulation, as well as the conformity of measurement results obtained on the territory of the Russian Federation with the results obtained in other countries.

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«PLANTS» CLUSTER FEATURES IN RM COLLECTION OF IGC SB RAS

Elena V. Shabanova[a], Irina E. Vasil'eva[a], Anna A. Zak[a], Dmitry S. Tausenev[b,]
Stefanie Scherbarth[c], Uwe Pierau[c] and Marina Y. Khomutova[a]

[a] A.P. Vinogradov Institute of Geochemistry of Siberian Branch of Russian Academy of Sciences, Irkutsk, Russia
ORCID: 0000-0002-6444-612X, e-mail: shev@igc.irk.ru

[b] OOO Sympatec, Ekaterinburg, Russia
[c] Sympatec GmbH, System-Partikel-Technik, Clausthal-Zellerfeld, Germany

Keywords: Certified Reference Materials, Plants, Traceability, Particle Distribution and Representative Sample

One of the ways to ensure the reliability of analytical data consumed in the study of regional and global biogeochemical processes is to use plant reference materials (RM) in order to calibrate analytical methods and control the accuracy of results. Despite the kind diversity of plants, the list of existing multi-element RM is very modest. Therefore, to ensure the accuracy and traceability of the results of determining a wide range of elements in plants by different analytical methods, the RM collection of IGC SB RAS (Russia) was added by the “PLANTS” cluster. It contains three certified reference materials (LB-1 birch leaf, GSO 8923-2007 / COOMET CRM 0067-2008-RU; Tr-1 mixture of meadow herbs, GSO 8922-2007 / COOMET CRM 0066-2008-RU; and EK-1 Canadian pond weed, GSO 8921-2007 / COOMET CRM 0065-2009-RU [1] and multi-element standard sample of pine needles HSS-1 (*Pinus sylvestris*) [2].

Each sample is a pollution indicator of natural terrestrial and aquatic ecosystems, since the choice of RM substance was based on such specific features of plants such as the ability quickly changing the elemental composition when the environment is polluted; a wide habitat area of growth; the possibility of selecting biomass sufficient for RM preparation. The features of plant materials include the structure of their stems and leaves, as well as the instability of organic matter during prolonged storage without decomposition.

As a result, the relationship between the shape, size and distribution of RM powder particles and the representative sample and the RM shelf life were studied.

The granulometric composition of RM powders that depends on the fibrous-splinter structure of plant powders was estimated by sieving on a standard set of sieves. The variations in the measurement conditions are limited the fibrous-splinter structure of plant materials, electrostatic particle adhesion, and their swelling in water. Later, the shapes and sizes of RM powder particles were studied using the QUICKPIC dynamic image analyzer with the RODOS/L dispersion module (Sympatec, Germany).

Particle size distributions in four RMs were performed via the diameter of a circle (EQPC) and Feret diameter (minimum / maximum). Although in RM powders, both spherical (the ratio of the perimeter of an equivalent circle to the real perimeter) and particles of other shapes are observed. Different variants of calculating the size of particles with low sphericity differ up to 5 times. In each case, the estimation of the shape, size, and particle distribution in RMs showed a decrease in the sphericity of organic matter particles with an increase in their size. The largest proportion of particles with a size of 1000-5000 microns is typical for CRM LB-1 when calculated using both methods. The particles of the powder from the RM of pine needles mainly are 1000-3800 microns. The particle size distribution affects the accuracy of estimating the uniformity of the distribution of elements in the substance and the mass of the representative sample (in the direction of its increase).

The representative sample of RM plants also depends on the method of sample preparation and chemical analysis. The possibility of reducing a representative sample for analytical methods using the transfer of a substance to a solution was established. According to the X-ray data, the representative weight is 1 g, and according to the ICP-AES data, it is 0.15-0.25 g, although most modern analytical methods operate with weights of no more than 0.1 g [3].

The shelf life of the RMs was established by monitoring the stability under natural aging conditions for 10 years using the results obtained by inductively coupled plasma atomic emission spectrometry, atomic absorption analysis with flame and electrothermal atomization, inductively coupled plasma mass spectrometry, X-ray fluorescence analysis and other methods. In the time interval between measurements was adopted for one year. The dependences of the error of certified contents on instability were established, and the values of the maximum possible changes in certified values from time to time were estimated. According to the tests carried out, the shelf life of the material of standard plant samples is 20 years.

The reference materials were certificated by ISO Guide 35:2006 [4]. Their metrological characteristics to be certified and the errors of certified values were established by interlaboratory experiment with participation of 20 qualified laboratories of Russia and COOMET member-countries. Element concentration of 41 (22), 38 (25), 34 (30) and 28 (12) are certified (recommended), respectively, in four plant samples from the CRM collection of the IGC SB RAS.

The traceability of certified contents of three CRMs was established by CRMs GWB07602-07605 GSV-1÷4 (leaves and branches of shrubs, poplar and tea) [5]. These CRMs were developed in China to ensure consistency of analytical data from various analytical methods when performing the "National-scale geochemical mapping project in China" [6]. The traceability of HSS was evaluated relative to LB-1, Tr-1, and EK-1 [2].

Thus, the "PLANTS" cluster of the CRM collection of the IGC SB RAS ensures the accuracy of the results of determining a wide range of elements by various analytical methods. The developed RMs are intended for performing chemical measurements during validation of existing and development of new methods of analysis, evaluation of traceability of results, and professional testing of laboratories of geological, agricultural, and pharmaceutical organizations [3, 4]. Their using for geoecological monitoring and biomedical research programs in order to assess the safety of medicinal plant raw materials will ensure consistency and reliability of analytical data from different chemical analysis methods.

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WORK ON PRODUCTION OF REFERENCE MATERIALS, EXECUTED JOINT-STOCK COMPANY «WESTERN-SIBERIAN TESTING CENTER» IN 2019-2020

Svetlana N. Shushunova

Joint-stock company «West-Siberian Testing Center»,Novokuznetsk, Russia
e-mail: main@zsic.ru , shushunova_sn@zsic.ru

Keywords: reference materials of coal, reference materials of mineral raw materials, West-Siberian Testing Center

Work on the production of reference materials has been started in the organization since 1986 and continues to the present time.

At present, 14 reference materials of Joint-stock company «West-Siberian Testing Center» have the status of approved types, GSO (reference materials of mining rocks, ores, coal, coke, ash and slag wastes), one reference material is included in the international register of COOMET (indicated in the table).

In recent years, Joint-stock company «West-Siberian Testing Center» continues to develop GSO coals of various ranks, intended for solving analytical problems of testing laboratories of Kuzbass and Russia, specializing in the analisis of coal samples.

During the last two years Joint-stock company «West-Siberian Testing Center» carried out the following works in the frame of production of reference materials:

- 2019 – developed and approved by GSO 11299-2019, GSO 11300-2019, reference materials of coal rank D, Zh (reference materials are analogues of GSO 8437-2003, GSO 9027-2008);
- 2020 – developed reference material of hard coal of rank T lean coal (RM-48) with a certified content of total sulfur of 0,73 %, the sample was successfully tested for the purpose of type approval at the UNIIM- branch of the Federal State Unitary Enterprize «All-Russian Scientific Research Institute for Metrology named after D.I. Mendeleev» (VNIIM), materials on the development of RM were transferred to Rosstandart for approval of the type of GSO.

At the moment Joint-stock company «West-Siberian Testing Center» is developing four state reference materials of coal (rank gas hard, antratsit, lean caking, candle).

On a sample of gas hard coal, the results of interlaboratory comprasion studies of one of the Russian Providers were obtained. An additional interlaboratory experiment is required to determine the mass fractions of total sulfur and phosphorus. By the end of this year, it is planned to send materials on this RM to UNIIM- branch of the Federal State Unitary Enterprize «All-Russian Scientific Research Institute for Metrology named after D.I. Mendeleev» (VNIIM) for testing for purpose of tipe approval. The approximate content of mass fraction of total sulfur in the developed sample is 0,5 %.

An interlaboratory experiment was carried out to determine the certified indicators of RM for coal of rank A, OS, D, in which 28 laboratories of Russia and the near abroad participated. In the first quarter of 2020, it is planned to send to the UNIIM- branch of the Federal State Unitary Enterprize «All-Russian Scientific Research Institute for Metrology named after D.I. Mendeleev» (VNIIM) materials according to RM data for testing for purpose of tipe approval.

For 2020-2021 it is planned to produse five reference materials of rank antratsit, lean coal, coking low-caking coal and jetcoal, two of wich have a hight content of total mass fraction of sulfur (about 1,0 and about 3,0 %).

In the testing laboratory of Joint-stock company «West-Siberian Testing Center» a set of statistical data on the assessment of the stability of the material and the certified characteristics of the operating reference materials is constantly being conducted.

Table 1. Information on the GSO composition of rocks, ores, coal, ash and slag wastes, developed by Joint-stock company "West-Siberian Testing Center"

No.	Description	Parameter	Duration of use
1	GSO 7221-96 Nepheline rock (RM-4)	Al_2O_3, CaO, MgO, TiO_2, Na_2O, K_2O, P_2O_5, MnO	without limitation
2	GSO 7222-96 Dolomite (RM -6)	SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO	without limitation
3	GSO 7223-96 Argillite (RM-11)	SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, Na_2O, K_2O, P_2O_5, MnO	without limitation
4	GSO 7224-96 Granite (RM-12)	SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O, K_2O, P_2O_5, MnO	without limitation
5	GSO 7460-98 Ash of hard coal (RM-1)	SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, Na_2O, K_2O, P_2O_5, Mn_3O_4, Co, Cr, Ni, Pb	until 2038
6	GSO 8488-2003 Gold-silver ore (RM-24), COOMET 0035-2005-RU	Au, Ag, Cu, Pb, Zn, Al_2O_3,TiO_2, MgO, K_2O	until 2023
7	GSO 11039 - 2018 (RM-45) Polymetallic ore of the Quartz Sopka field	Pb, Zn, Cu, BaO, As, Cd, Co, Ni, TiO_2, Al_2O_3, SiO_2, $Fe_2O_{3\ total.}$, S_{total}, MnO, CaO, MgO, Na_2O, K_2O, Au, Ag	until 2028
8	GSO 10230-2013 Coal coke (RM-40)	A^d (ash), S_t^d (sulfur total), P^d (phosphorus), K_2O (potassium oxide in ash), Na_2O (sodium oxide in ash)	until 2023
9	GSO 10893-2017 Hard coal of rank GZhO, gas fat lean hard coal (RM-41)	A^d (ash), S_t^d (sulfur total), d_r^d (true density)	until 2022
10	GSO 10894-2017 Hard coal of rank OS, lean caking coal (RM-42)	A^d (ash), S_t^d (sulfur total), d_r^d (true density), V^d (volatile matter)	until 2022
11	GSO 10895-2017 Hard coal of rank G, gas hard coal (RM-43)	A^d (ash), S_t^d (sulfur total), d_r^d (true density), P^d (phosphorus)	until 2022
12	GSO 10896-2017 Hard coal of rank T, lean coal (RM-44)	A^d (ash), S_t^d (sulfur total), d_r^d (true density), P^d (phosphorus), V^d (volatile matter)	until 2022
13	GSO 11299-2019 Hard coal of rank D, jetcoal (RM-46)	A^d (ash), S_t^d (sulfur total), d_r^d (true density), P^d (phosphorus)	until 2024
14	GSO 11300-2019 Hard coal of rank Zh, fat coal (RM-47)	A^d (ash), S_t^d (sulfur total), d_r^d (true density), P^d (phosphorus)	until 2024

DEVELOPMENT OF CERTIFIED REFERENCE MATERIALS FOR MEASURING PRIORITY ORGANOTIN COMPOUNDS IN MATERIALS AND ENVIRONMENTAL OBJECTS

Vadim V. Smirnov, Anatoly I. Krylov. Mikhail V. Belyakov, Irina.Ju. Tkachenko

D.I. Mendeleyev Institute for Metrology, Saint Petersburg, Russia
ORCID 0000-0001-7380-4649, e-mail: smirnov@b10.vniim.ru

Keywords: analytical chemistry, CRM certification, organotin compounds, HPLC-ICPMS, mass spectrometry, traceability, ecology

In connection with the increasing attention to the protection of the environment from anthropogenic pollution, in recent years, considerable interest has been directed to the determination of organotin compounds in natural objects, first of all, in soils and sediments. According to the order of the Government of the Russian Federation of December 30, 2015 No. 2753-r [1], organotin compounds in the soil are included in the list of pollutants, the determination of the content of which becomes necessary during dredging.

International standard ISO 23161 [2] provides for the definition of a number of priority organotin compounds in soils. In accordance with this standard, calibration solutions can be prepared from pure commercial substances of analytes that do not have traceability to any standards. Existing organotin CRMs in various matrices (PACS-2, SOPH-1 - NRC, Canada; BCR-462, BCR-477, BCR-646 - IRMM, Belgium, etc.) make it possible to control the accuracy of the analysis performed and traceability for some from the list determined according to ISO 23161, thus it is obvious the need to create a standard sample of a mixture of the main priority organotin compounds.

The traditional method for certifying pure substances is the mass balance method (100% minus impurities). To do this, determine the content of impurities from the main groups: water, volatile organic compounds, inorganic compounds and related compounds.

In the process of determining impurities of related compounds, it was found that the method of high performance liquid chromatography with detection on an inductively coupled plasma mass spectrometer (HPLC-ICPMS) is the most suitable for these purposes, since when carrying out sample preparation for the method of gas chromatography with mass spectrometry (GC-MS), which includes the stages of extraction and derivatization, part of the basic substance undergoes degradation, with the formation of new related impurities, and there is also a significant influence of the background, and a relatively high component of uncertainty by type A. An example of a chromatogram for the determination of impurities (triphenyltin chloride), obtained by HPLC-ICPMS, is shown in Figure 1

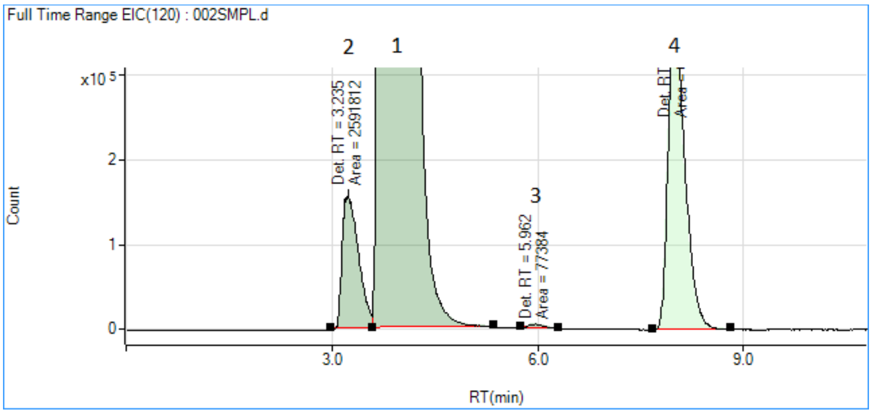

Fig. 1. An example of a chromatogram obtained by HPLC-ICPMS in the determination of related impurities in triphenyltin chloride. 1 - triphenyltin chloride. 2,3,4 - impurities of related organotin compounds

For the manufacture and certification of reference materials of priority organotin compounds, pure organotin substances were investigated and certified. Certification of pure substances was carried out on the equipment that is part of the state primary standard (National Standards) GET 208. The declared purity and the results of certification of substances are shown in Table 1.

Table 1. The purity of the starting materials and the results of their certification for GET 208

Substance	**Commercial product, declared purity,%**	**Certification results**	
		Purity assay, %	Extended uncertainty, %
Monobutyltin trichloride	95,0	99,49	0,14
Dibutyltin dichloride	96,0	95,33	0,76
Tributyltin chloride	96,0	98,60	0,24
Monooctyltin trichloride	-	96,76	0,15
Dioctyltin dichloride	-	96,36	0,18
Triphenyltin chloride	95,0	97,29	0,42
Tricyclohexyltin Chloride	95,0	99,19	0,14
Tetrabutyltin	93,0	90,80	0,65

As part of the work carried out, sets of documents were developed, a pilot batch of certified reference material was manufactured and released. Certified reference material are registered in the state register of approved types of reference materials under the numbers 11410-2019 and 11411-2019. The characteristics of the CRM are shown in Table 2.

Table 2. Metrological characteristics of the developed certified reference materials

CRM number	**Index of RM**	**The name of the certified characteristics**	**The range of permissible certified values of the mass concentration of individual organotin cations, mg/cm^3**	**Certified value of mass concentration of an experimental batch of CRM, mg/cm^3**
11410-2019	7ООС-ВНИИМ	mass concentration of cation monobutyltin in methanol	0,08 ÷ 0,12	0,096
		mass concentration of cation dibutyltin in methanol	0,08 ÷ 0,12	0,105
		mass concentration of cation tributyltin in methanol	0,08 ÷ 0,12	0,107
		mass concentration of cation monooctyltin in methanol	0,08 ÷ 0,12	0,111
		mass concentration of cation dioctyltin in methanol	0,08 ÷ 0,12	0,110
		mass concentration of cation triphenyltin in methanol	0,08 ÷ 0,12	0,099
		mass concentration of cation tricyclohexyltin in methanol	0,08 ÷ 0,12	0,105
11411-2019	ООС-ВНИИМ	mass concentration of tetrabutyltin in isooctane	0,8 ÷ 1,2	1,01
The relative expanded uncertainty U at k = 2 (P = 0.95) for all the given values is 3%				

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2. ISO 23161:2009 - Soil quality - Determination of selected organotin compounds - Gas-chromatographic method.

PURITY ASSESSMENT OF POTASSIUM IODATE BY COULOMETRIC TITRATION AND BY THE ANALYSIS OF IMPURITIES

Alena V. Sobina, Egor P. Sobina, Alexander Y. Simolin

UNIIM - Affiliated Branch of the D.I.Mendeleev Institute of Metrology, Ekaterinburg, Russia
e-mail: sobinaav@uniim.ru

Keywords: purity of salts, potassium iodate, mass fraction of the main component, coulometric titration, mass fraction of impurities, primary standard, metrological traceability

Purity assessment of salts is the important issue of metrological traceability in relation to the nonmetallic elements and metals, unstable in air (alkaline and alkaline-earth), since the source substances for the preparing the certified reference materials (CRMs) of calibration solutions of such elements are salts. Potassium iodate with a known content of the main component can act as a source for the preparation of CRMs of calibration solutions of iodine, as well as can be used in elemental analysis to ensure traceability for measurement results of potassium, iodine and oxygen content. The purpose of this study was to determine the mass fraction of the main component (potassium iodate), the mass fraction of the base elements (potassium, iodine and oxygen) in the commercially available pure salt of potassium iodate to create a primary standard (hereinafter PRM) by two approaches: by direct (the measured value is measured directly) and indirect (the content of impurities is determined and then purity is calculated as 100% minus the sum of impurities).

The method of coulometric titration was used to measure the mass fraction of potassium iodate in the candidate material of PRM using a standard installation that is a part of the State primary standard of the units of the mass (molar, atomic) fraction and mass (molar) concentration of components in liquid and solid substances and materials based on coulometry GET 176-2019, according to the measurement procedure described in [1]. The measurement result obtained as the arithmetic mean of nine replicates is shown in Table 1. Since the used measurement technique allows to measure the amount content of all oxidants in the analyzed substance, the absence of other oxidants except iodate ion was previously confirmed by ion chromatography. Investigations of the homogeneity, long-term and short-term stability of the candidate material of PRM of potassium iodate were also performed by coulometric titration.

The mass fraction of 71 impurities in the candidate material of PRM of potassium iodate was measured using inductively coupled plasma mass spectrometry and ion chromatography. To assess the purity of potassium iodate (i.e., the mass fraction of the main component) based on the analysis of impurities, the approaches described in [2, 3] were used, taking into account the mass balance equation, ionic form of the impurities present and the principle of electroneutrality. The results are shown in Table 1.

According to the Table 1, the values of the mass fraction of potassium iodate, obtained by coulometric titration and by the analysis of impurities, are in good agreement with each other. This fact is considered to confirm the adequacy of the model used to estimate the purity of the salt by indirect approach based on the analysis of impurities and the correctness of the developed by UNIIM measurement procedure for the mass fraction of potassium iodate by coulometric titration, as well as the algorithms used for estimating the uncertainty of measurement results based on GUM [4].

The candidate material of PRM of potassium iodate was used as a sample in the key comparison and parallel pilot study CCQM-K152/P192 “Assay of potassium iodate” coordinated by UNIIM in 2018-2020. Participants of these comparisons were the national metrological institutes of Russia, China, Japan, Slovakia, Turkey, Brazil, Mexico, Argentina, and Poland. The key comparison reference value (KCRV) for the amount content of oxidants expressed as potassium iodate is 4.67194 mol/kg with the expanded uncertainty (k=2) 0.00050 mol/kg, which corresponded to mass fraction of potassium iodate value of (99.980±0.006) %. The KCRV for the mass fraction of iodine in potassium iodate is 0.59291 kg/kg with an extended uncertainty (k=2) of 0.00010 kg/kg. So for both measurands there is a good agreement of the values from the key comparison with the measurement results given in Table 1.

Table 1. Measurement results for the mass fraction of the main component in the candidate material of PRM of potassium iodate obtained by the method of coulometric titration and by the analysis of impurities

Measurand and units of measurement	**Approach**	**Measurement method (s)**	**Measurement result, %**	**Expanded uncertainty (k=2), %**
Mass fraction of potassium iodate, %	Direct	Coulometric titration	99.969	0.024
	Indirect (100% minus sum of impurities)	Inductively coupled plasma mass spectrometry, ion chromatography	99.976	0.010
Mass fraction of potassium, %			18.256	0.010
Mass fraction of iodine, %			59.290	0.012
Mass fraction of oxygen, %			22.425	0.010

The results of the work performed are the follows:

- the measurement results of mass fraction of the main component in the candidate material of PRM of potassium iodate by the direct approach using the primary method of coulometric titration and by indirect approach based on the analysis of impurities using the methods of mass spectrometry with inductively coupled plasma and ion chromatography were obtained;

- comparing of results between themselves and with the reference value of the international key comparison CCQM-K152 has shown that the results are in good agreement;

- metrological characteristics of the primary standard of potassium iodate PRM-1.1-176-023-2018-KIO_3 were determined. This PRM is intended for storing and transferring the unit of mass fraction of the component reproduced by the State primary standard GET 176-2019, and can be used to prepare CRMs of iodine calibration solutions as well as to ensure metrological traceability of the measurement results of potassium, iodine or oxygen content in elemental analysis.

The use of direct and indirect approaches simultaneously to determine the mass fraction of the main component and the mass fraction of the base elements in the pure salt is an effective (although very labor-intensive) tool for investigating the metrological characteristics of PRMs and for validating newly developed measurement procedures for reproducing units of component content using GET 176-2019.

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THE PROSPECTS FOR IMROVING OF STATE PRIMARY MEASUREMENT STANDARD FOR UNITS OF SPECIFIC GAS ADSORPTION, SPECIFIC SURFACE AREA, SPECIFIC PORE VOLUME AND PORE SIZE, OPEN POROSITY AND GAS PERMEABILITY COEFFICIENT

Egor P. Sobina

UNIIM – Affiliated Branch of the D.I. Mendeleyev Institute for Metrology, Eekaterinburg, Russia
ORCID: 0000-0001-8489-2437, e-mail: 251@uniim.ru

Keywords: porosity, gas permeability coefficient, specific surface area, specific pore volume, pore size, standard, reference material, metrological traceability

The most important characteristics of the structure of porous and dispersed substances and materials are specific surface area, specific pore volume, pore-size, open porosity, and gas permeability coefficient. The adsorption capacity of absorbents, the efficiency of solid catalysts and the characteristics of the filter material depend on these properties. The specific surface area of active carbons is comprised between 500 and 1500 m^2/g; of silica gel it's up to 800 m^2/g; of macroporous ion-exchange resins is no more than 70 m^2/g; of diatomite carriers for gas-liquid chromatography is less than 10 m^2/g; of non-porous metal and ceramic powders is less than 1 m^2/g; as for rocks, the maximum of its' open porosity variation is comprised between 3 and 50 % and the range of gas permeability coefficient is $(10^{-3}$-$5)\ \mu m^2$. [1-5]. For the metrological measurement assurance of porosity and permeability in 2019 was approved GET 210-2019 – State primary standard for units of specific gas adsorption, specific surface area, specific pore volume, pore size, open porosity, and gas permeability coefficient of solids and materials.

However, in practice, there are measurements of the porosity and permeability characteristics that have not had yet developed metrological assurance both in Russia and abroad. In this regard, this paper analyses the most popular areas of improvement of the state primary standard.

Nowadays, the topic of the prospect of shale gas and oil accumulation development is the most discussed and relevant in gas business which solids are characterised by low values of gas permeability coefficients - $(1\cdot10^{-8}$- $1\cdot10^{-3})\ \mu m^2$. Economical efficiency and production cost of gas and oil recovery crucially depend on measurement accuracy of gas permeability coefficient. It is no longer possible to use the stationary filtration method to make measurement of low values of the coefficient because gas flow is too low. For measurements in practice, the method of non-stationary filtration is used, in which the flow rate is indirectly calculated from the pressure drop. At present, there is absolute lack of metrological measurement assurance of such low values of gas permeability coefficient in Russia and abroad to fulfill the requirements of the Order of the Ministry of natural resources of Russia dated 15.05.2014 No. 218, which provides for monitoring the porosity and gas permeability of rocks in accredited laboratories.

The second urgent task is development of metrological measurement assurance of permeability of liquid for rocks, sintered metal materials, soils and building materials.

The third task that can be singled out is development of metrological measurement assurance of the size of large pores ($D>70\ \mu m$), what is relevant for ceramic water purification filters.

The fourth task includes metrological assurance of oxygen, water vapor, and carbon dioxide permeability measurements for evaluating the barrier properties of polymer wraps, bags, and containers used as packaging in the food and pharmaceutical industries.

The fifth task includes metrological measurement assurance of air permeability of textiles, non-woven materials, paper, filters, membranes, and films.

The sixth task includes metrological measurement assurance of catalysts efficiency parameters by the method of chemosorption, e.g., the catalyst of Pt/Al_2O_3 by method of chemical adsorption of hydrogen in pulsed action with the ability to measure parameters such as: the amount of gas that reacts with the metal, the specific surface of the metal, the degree of dispersion of the metal.

All the designated issues of metrological assurance can be solved by including into GET 210-2019 additional reference installations of various constructions depending on analysed materials and development of new national reference materials with their usage. Work on improvement of GET 210-2019 for solving the first task is already planned for years of 2021-2023. The fast solving of the 2-6 issues is possible only with the base of state-private partnership in the framework of improving GET 210-2019. The driving component of GET 210-2019 improvement is the requests of consumers: choice of priority areas will be defined by analysis of official letters that should include requirements of metrological assurance improvement of porosity and permeability of solid substances and materials. Development of new reference materials will provide metrological assurance of measuring instruments for porosity and permeability parameters in the considered areas, at the same time, Russian metrology will be independent and all of these factors could realize policy of import substitution of expensive foreign reference materials.

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CURRENT STATE OF THE REFERENCE MATERIALS TESTS FIELD. STANDARD SUBSTRUCTION OF UNIIM FOR METROLOGICAL TRACEABILITY ASSURANCE

Egor P. Sobina, Sergei V. Medvedevskikh, Olga N. Kremleva

UNIIM – Affiliated Branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
ORCID: 0000-0001-8489-2437, e-mail: 251@uniim.ru
ORCID: 0000-0002-6003-040X, e-mail: kremleva@uniim.ru
ORCID iD: 0000-0003-3084-1612, e-mail: uniim@uniim.ru

The year of 2020 is the year of challenges and events, year of of extreme conditions and a new reality, the year that has set new tasks in the global scale. The issues of development and application of reference materials did not lose high level of relevance even in this difficult time. Past 2019 showed and the current year confirmed involvement of RMs in all areas of activity which has the measurement process. Modern tendencies in the field of metrological traceability assurance, increased requirements to demonstration of metrological traceability of measurements assign a large and significant role to the creation of the necessary nomenclature of RMs which have reasonable and reliable metrological traceability to state or foreign primary standards of units.

The unique system is created, developed and acting from 1970-s called State Service of Reference Materials for composition and properties of substances and materials, connecting reference materials producers with not only RMs consumers but also federal executive bodies. The certification of reference materials types with purpose of admission to use in the sphere of state regulation of uniformity of measurement assurance is regulated by state regulatory legal acts. Nowadays, there are about 4,000 acting certified reference materials in the Russian Federation. The understanding the method, mechanism, and commitment to establish and demonstrate of metrological traceability of certified value of RMs had been advancing dynamically since the entry into force of the main law for uniformity of measurement assurance in the Russian Federation (Federal Law №102-FZ dated 26 June 2008 «On assurance of uniformity of measurements») and now we see that the demonstration of metrological traceability is absolutely different from the ones which were applicated in RM data sheets, e.g. dated 2010. The implementation of new regulatory legal acts in Russia as well as requirement toughening for formulation and demonstration of metrological traceability of metrological assurance instruments are both making their own adjustments to procedure of RMs production which are traceable to state primary standards according to State verification schedules. Despite the «law isn't retrospective», significant part of RM producers is updating documents regularly, including metrological traceability demonstration, both in terms of formulations clarifying, and in terms of methods of RMs characterisation. For those exceptional types of measurements that do not have a state primary standard at the head, the issue of creating primary reference measurement procedures or local verification schemes is being considered.

Currently, Russian institutes for metrology have rich base of primary, secondary and working standards for units, that is implementing almost complete «coverage» of measurement types related to sphere of state regulation for uniformity of measurement assurance.

UNIIM – Affiliated Branch of the D.I. Mendeleyev Institute for Metrology is holder for 10 state primary and 3 secondary standards. According to state verification schedules, base of standards of UNIIM is able to provide the production of manufactured RMs as well as development of new traceable RMs for which non-organic components containing, physical properties such as sorption properties, porosity, permeability, magnetic properties, thermophysical properties, etc. The report includes base of standards of UNIIM, nomenclature of manufactured RMs and also main directions of its improvement.

DEVELOPMENT AND TESTING OF A MULTI-ELEMENT ICP STANDARD

Tatyana P. Stolboushkina, Alexey A. Stakheev

All-Russian Scientific Research Institute of Physical Technical and Radio Technical Measurements
Moscow region, Mendeleevo, Russia
e-mail: mera@vniiftri.ru

Keywords: inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectroscopy, aqueous solution, standard, water analysis, inorganic component, ICP

Inductively coupled plasma spectrometers are widely used for elemental analysis of more than 70 elements. These methods are the most express, highly sensitive methods for qualitative and quantitative analysis. Like many other methods of chemical analysis ICP methods need calibration. The ICP calibration procedure requires the employment of standards whose values and their associated uncertainties are known and established following a metrological procedure. The accuracy of measurements a strongly depends on the quality of CRM and, therefore, their characterization and traceability is very important. RM's are solutions with a certain value of the mass fraction or mass concentration of one or another element of the periodic system.

Russian metrological Institute of technical physics and radio engineering (VNIIFTRI) is working on the development and testing in order to approve the type of reference materials for inductively coupled plasma methods (ICP - RM). The comparability of measurement results in analytical and industrial laboratories is ensured by the traceability of ICP-RM to the State primary standard of units of mass fraction and mass (molar) concentration of inorganic components in aqueous solutions based on gravimetric and spectral methods GET 217-2018.

One of the main advantages of the ICP - MS and ICP - OES methods is the ability to quickly and simultaneously measure a large number of elements in samples, which is feasible only when using multi-element reference materials since their application greatly simplifies and accelerates the process of preparing calibration solutions. VNIIFTRI is working on the development of a multi-element reference materials of the mass fraction of metals in solution which will allow calibration of measuring instruments for the simultaneous determination of several elements by inductively coupled plasma (ICP - RM Multi) for metrological support of high-precision methods.

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METROLOGICAL ASSURANCE OF ENZYME MULTIPLIED IMMUNOASSAY. CURRENT STAGE AND DEVELOPMENT PROSPECTS

Valeria V. Studenok, Maria Yu. Medvedevskykh, Anna S. Sergeyeva

UNIIM – Affiliated Branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
ORCID: 0000-0002-3363-3133, e-mail: studenok@list.ru

Keywords: Nutrition products, technical regulations, measurement procedure, assay, enzyme multiplied immunoassay, reference materials

Enzyme multiplied immunoassay (EIA) is high-sensitive and high-specific method of laboratory research based on antigen-antibody reaction which detection is realized due to enzymatic labelling with its subsequent detection by means of proper substrate changing its' stain [1]. EIA is one of the most actively developing directions of chemical enzymology both in Russia and abroad. The procedure of EIA is constant developing. In one hand, the number of objects under study is increasing, on the other hand, the methods of the analysis are being deepened and improved. The continuous search for more and more new enzymes used as markers is underway. EIA methods have widely entered to analytical practice and now are used in various spheres of medical science, agricultural sector, microbiological and nutritive industries as well as for environmental control purposes.

Nowadays is actively developing the assays which could let performance of quality detection with further quantitative measurement of the following substances: food-borne allergens (gluten, milk powder, nuts, egg albumen, soy), myconotoxins, anticoccidials, antibiotics, pesticides, growth-promoting hormones, etc. All these substances are included into list of safety indicators of technical regulations of the Customs Union which establishes requirements to nutrition products. Existing standard and certified procedures included into list of the Technical regulations are mainly based on methods of chromatography. However, the high cost of equipment and used reagents, reference materials, and also high requirements for qualification of personnel, in total limit implementation of such methods in testing laboratories of both productions plants and organisations carrying disease and surveillance control. Usage of screening EIA procedures will allow optimise outlays of laboratories and provide high quality of measurements when the accordance of nutrition products and food staples safety indicator to necessary requirements (from Technical regulations) is stated. Development and certification of measurement procedures based on usage of EIA testing systems is necessary for assurance of legislative requirements in the field of technical regulations [2]. Nowadays, there is no a unified metrological approach for realisation of submission to appliance of reappeared screening procedures. considering the specifics of EIA method, existing approach to attestation of procedures of qualitative chemical assay requires improvements. In this connection, development of metrological measurement assurance complex performed by EIA method is relevant. This complex should include next procedures:

1) Development of high-precision (if necessary, reference) analysis methods intended to establish the metrological characteristics of rapid methods, as well as, further, to establish the characteristics of reference materials;

2) Methodological assistance to developers and (or) organisations that distribute assay systems in the Russian Federation in terms of the preparation of methodology and methods for presenting of metrological characteristics;

3) Development of necessary nomenclature of reference materials for results control got with usage of test systems;

4) Performance of interlaboratory comparison tests on the stages of:

- approval of methodology (installation of accuracy indices);

- implementation of methodology (functional check of methodology) for different categories of laboratories and products;
- proficiency testing of laboratories that use this methodology in the framework of preparation for accreditation;

5) Coworking with technical committee on standardisations on the stage of methodology preparation as standard, and also carrying of metrological examination.

Since 2016 specialists from UNIIM are carrying works on metrological assurance of the EIA with implementation of existing instrumental and etalon base. State secondary standard for units of mass fraction and mass (molar) concentration of organic compounds in liquid and solid substances and materials on the base of gas and liquid chromatography GVET 208-1-2016 is used for detection of mass fraction of high-purity substances parent material (antibiotics, pesticides, micotoxins) that are used for preparation of calibration solution. There is a prospect of existing possibility of usage of GVET 208-1-2016 for setting of amino acid composition. Detection of nitrogen (protein) mass fraction in reference materials is carrying by State secondary standard for units of mass fraction and mass (molar) concentration in liquid and solid substances and materials on base of volumentary titration method of analysis GVET 176-1-2010; determination of moisture mass fraction is carrying on State primary standard for units of mass fraction and mass (molar) concentration of water in solid and liquid substances and materials GET 173-2017. For attestation of the procedure is used immunologic analyser Multiskan FC by «Thermo Scientific» and also general laboratory equipment for implementation of EIA such as non-automatic scales, test-tube centrifuge, shaker, bath chamber, autoproportioner, volumetric ware.

The examples of practical appliance of proposed scheme of EIA measurement procedure integration into the field of technical regulating are researches carried by UNIIM specialists cooperated with Xema-Medica Co. Ltd on the development of metrological assurance for milk powder in drinking milk [3].

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TRACEABILITY OF MEASUREMENTS OF MECHANICAL STRESSES BY ACOUSTOELASTIC METHOD BASED ON REFERENCE MATERIAL

Vladimir V. Tolmachev, Ilona N. Matveeva

UNIIM – Affiliated Branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
e-mail: sertif@uniim.ru

The study of the stress-strain state (hereinafter - SSS) is an urgent task in the manufacture and assessment of the resource of mechanical engineering products, pipelines, vessels and building structures for various purposes and their elements.

An analysis of the federal information fund of approved types of measuring instruments showed that, as of 2020, there are measuring instruments of an approved type that implement the following methods of controlling SSS - acoustic, electric, magnetic, free vibration method.

Measuring instruments (hereinafter referred to as MI), which implement the acoustic method of controlling SSS, are included in the register as a means of measuring mechanical stresses. However, due to the absence of a standard of mechanical stresses for these measuring instruments, metrological traceability is not provided.

UNIIM - a branch of the Federal State Unitary Enterprise “VNIIM named after D.I. Mendeleev” conducted tests to approve the type of a set of certified reference materials of mechanical properties of steels (set INCO MSS-MN 1) - GSO 11544-2020 / GSO 11545-2020.

The metrological characteristics of GSO 11544-2020 / GSO 11545-2020 are presented in tables 1, 2.

Table 1 - Standardized metrological characteristics of SO-800 (GSO 11545-2020)

Certified characteristic	Unit designation	Interval of certified values	The limits of the admissible values of the absolute error of the certified value at a confidence level 0,95, (± Δ)
mechanical stress σ_{pl}, proportional limit*	MPa (N/mm^2)	480-830	± 22
mechanical stress $\sigma_{0,2}$, conditional yield stress with a tolerance for the amount of plastic deformation 0.2%*	MPa (N/mm^2)	600-1020	± 22
mechanical stress $\sigma_в$, tensile strength*	MPa (N/mm^2)	700-1200	± 22
Stress increment with 1% incremental elongation (modulus of elasticity) E *	MPa (N/mm^2)	1650-2000	± 50
* The names of the certified characteristics correspond to [1]			

A distinctive feature of the developed certified reference materials is certification according to the characteristics "Stress σ_{pl}, proportionality limit", "modulus of elasticity E". The certified values of these characteristics make it possible to more accurately set the loading steps in the elastic deformation region when establishing the elastic-acoustic coupling coefficients according to [2].

The set consists of samples of a special design, which provides the possibility of installation in grips of tensile and universal testing machines.

The initial material for the production of certified reference materials was a rolled sheet made of structural steel, forging made of high-quality structural high-alloy steel.

Due to the fact that the value of the intrinsic acoustic anisotropy of the material is an important characteristic in the implementation of the acoustic method of controlling the stress-strain state, the initial material was investigated in terms of intrinsic acoustic anisotropy by the method [3]. The starting material was found to be isotropic.

The establishment of the certified values CRM and the estimation of the error of the certified values were carried out in accordance with the algorithms [4]. When calculating the errors of the certified values, the results of evaluating the homogeneity were taken into account.

The estimation of homogeneity was carried out in accordance with [4].

Expiration date of the CRM set is established as expiration date of similar CRM mechanical properties of steels (GSO 10957-2017). The expiration date CRM is 10 years.

The traceability of the certified values to the measurement unit is realized through direct measurements on the State standard of force unit in accordance with the State verification scheme for force measuring instruments, the State verification scheme for length measuring instruments in the range from 1 10-9 to 100 m and wavelengths in range from 0.2 to 50 microns.

The development and application of GSO 11544-2020 / GSO 11545-2020 mechanical properties of steels allows:

- carry out tests in order to approve the type of mechanical stress measuring instruments using the acoustoelastic method;
- carry out verification and calibration of mechanical stress measuring instruments using the acoustoelastic method;
- to control the accuracy of the results of measurements of mechanical stresses.

For the application of GSO 11544-2020 / GSO 11545-2020 when measuring SSS by acoustical, electrical, magnetic and other methods, it is necessary to develop and certify the corresponding measurement techniques.

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PLANT-MATRIX CERTIFIED REFERENCE MATERIALS – A TOOL FOR ENSURING THE UNIFORMITY OF CHEMICAL MEASUREMENTS

Irina E. Vasileva, Elena V. Shabanova

A.P. Vinogradov Institute of Geochemistry of Siberian Branch of Russian Academy of Sciences,
Irkutsk, Russia
ORCID: 0000-0001-6315-083X, e-mail: vasira@igc.irk.ru

Keywords: plant-matrix certified reference materials and reference materials, elemental composition, methods of chemical analysis, ensuring the uniformity of measurements, manufacturers of plant reference materials

Plants contain almost all the chemical elements of the Periodic table of D. I. Mendeleev, reflect the relationship between living and inanimate nature, and participate in the biogeochemical cycle of substances on Earth [1]. To study the patterns of changes in the natural environment, it is important to obtain reliable chemical information about the plant world [2, 3]. Traditionally, plants are considered from two positions: human consumption (use of plants for food, clothing and technical fabrics; construction; energy; medicine and chemistry) and the impact of human activity on the environment (environmental aspect).

The report discusses the role of certified reference materials (CRM), reference materials (RM), samples for quality control (QC) of plant materials as a tool that ensures the unity of measurements and reliability of results in environmental research, production of food and medicinal plant raw materials and drug products [3, 4]. Features of plant composition as objects of chemical analysis and requirements for methods of its determination are considered from the point of view of providing reference materials for traditional agricultural tasks, geochemical, environmental and biomedical projects. International and Russian regulatory documents on the development of RMs and the normalized content of toxic elements in plant-matrix materials are presented. A brief history of the creation of cultivated and natural plant reference materials by leading manufacturers of CMRs is given. The number and types of plant materials developed by producing organizations from different countries are presented as of 01.03.2020. Different filling of classes of existing certified, reference and quality control samples of plant materials from different manufacturers is noted. Providing analytical research with information about the elemental compositions of reference materials from the electronic databases "ARSHIN", COMAR and GeoREM is discussed. The necessity and prospects of expanding the list of matrix reference samples to ensure the reliability and comparability of the results of chemical analysis of plants, food products, medicinal plant raw materials and products made from them (dietary supplements, powders, tablets, tinctures, herbal decoctions and others) are shown.

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AUTOMATION OF THE PROCESS OF PROCESSING THE RESULTS OF PARTICIPATION IN PROFICIENCY TESTING SCHEME

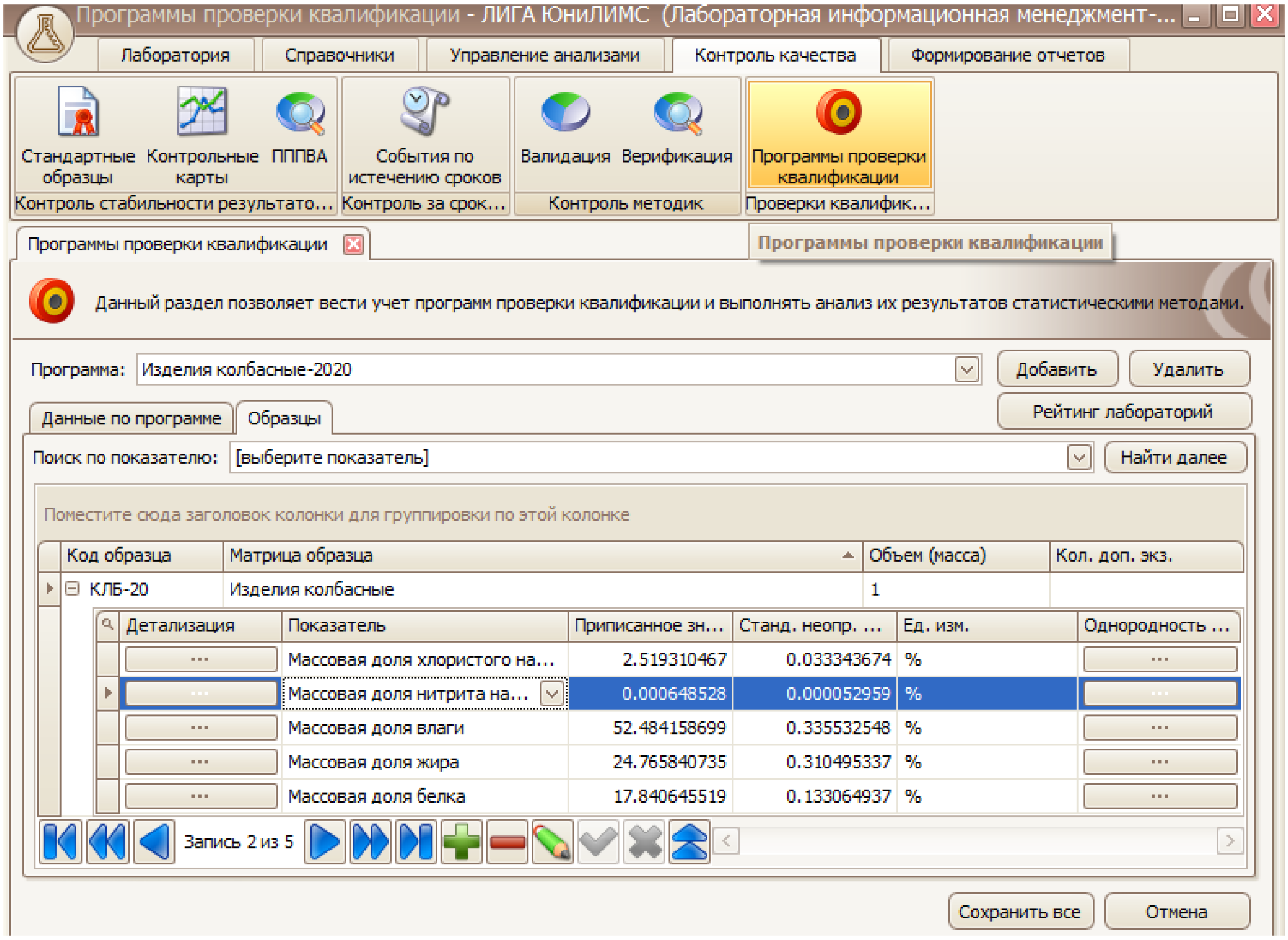
Ekaterina V. Vasina, Elena U. Fritsler

LLC “CMCT “KOMPETENTNOST”, Samara, Russia
e-mail: 2312387@mail.ru

Keywords: proficiency testing, interlaboratory comparison, proficiency testing provider, proficiency testing scheme, robust statistical method, software, coordinator

In their activities, proficiency testing provider checks work with a large amount of information received from the participants of the interlaboratory comparison. Coordinator perform complex statistical calculations based on GOST P 50779.60-2017 (ISO 13528:2015), GOST ISO/IEC 17043-2013, GOST P ISO 5725-2002 part 1-6. If there are a small number of interlaboratory comparison participants, it is possible to process information in MS Office Excel. There is still a risk of technical errors associated with transferring formulas.

When the number of interlaboratory comparison participants increases, as well as due to the need to perform calculations using robust statistical method, the proficiency testing provider LLC “CMCT “KOMPETENTNOST” , has a need to hard-program the formulas and mechanisms described in GOST P 50779.60-2017 (ISO 13528:2015), GOST ISO/IEC 17043-2013.



Данный раздел позволяет вести учет программ проверки квалификации и выполнять анализ их результатов статистическими методами.

Программа: Изделия колбасные-2020

Поиск по показателю: [выберите показатель]

Код образца	Матрица образца	Объем (масса)	Кол. доп. экз.
КЛБ-20	Изделия колбасные	1	

Детализация	Показатель	Приписанное зн...	Станд. неопр. ...	Ед. изм.	Однородность ...
...	Массовая доля хлористого на...	2.519310467	0.033343674	%	...
...	Массовая доля нитрита на...	0.000648528	0.000052959	%	...
...	Массовая доля влаги	52.484158699	0.335532548	%	...
...	Массовая доля жира	24.765840735	0.310495337	%	...
...	Массовая доля белка	17.840645519	0.133064937	%	...

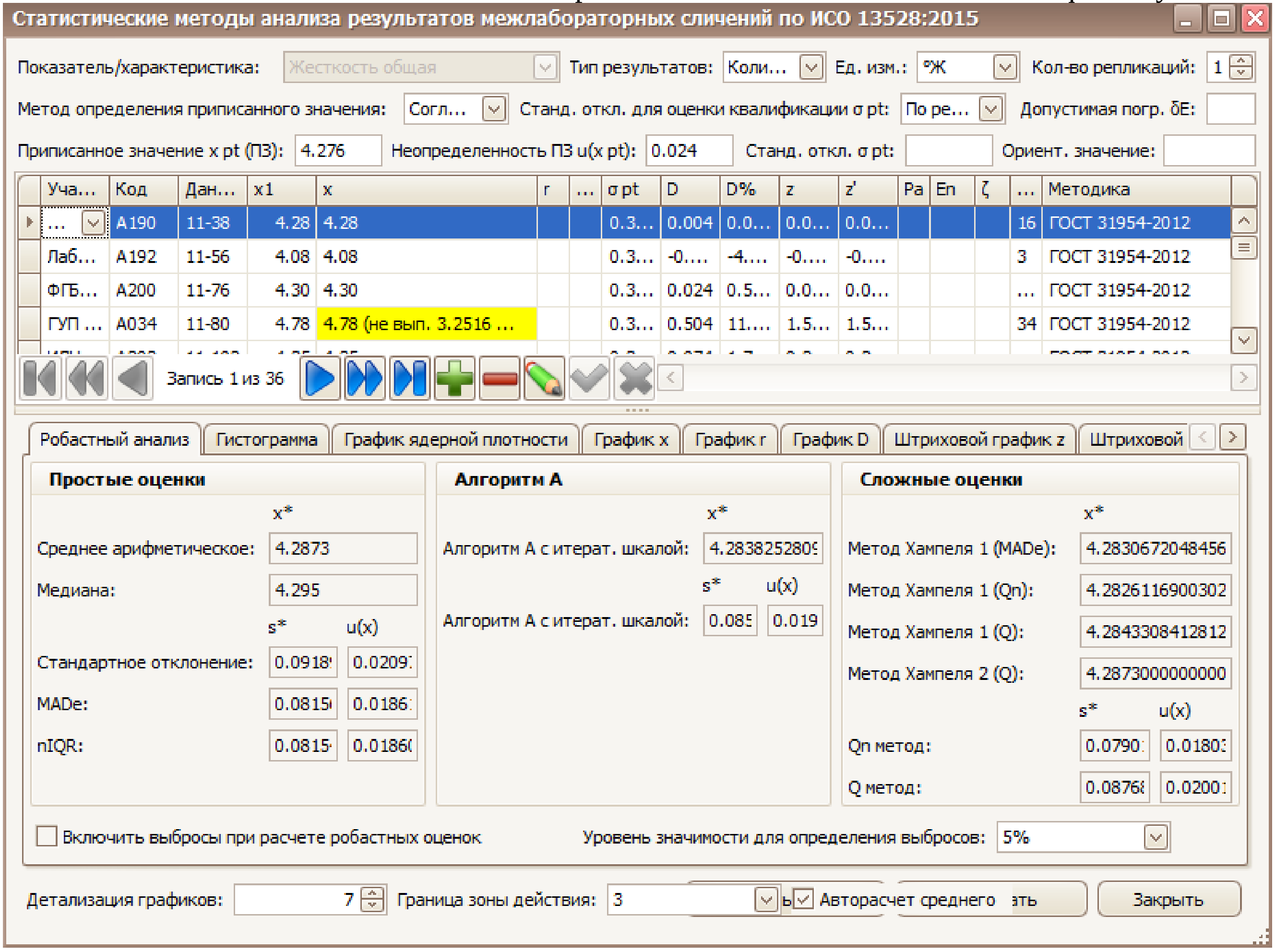
Fig 1. Example UniLIMS

For this purpose, in 2017, a technical task was formed, which was passed to our partners JSC "Liga"for implementation. Employees of JSC "Liga" added the "proficiency testing scheme" block to the existing laboratory information management system "UniLIMS".

The use of the block "proficiency testing scheme software "UniLIMS" allowed:

- to exclude technical errors associated with the transfer of the formulas;
- perform complex statistical calculations using robust statistical method (all methods described in GOST P 50779.60-2017 (ISO 13528:2015));
- to automate the calculations of homogeneity/stability of proficiency test item;
- perform calculations of performance indices in all ways GOST P 50779.60-2017 (ISO 13528:2015);
- minimize the labor costs of coordinator;
- automatically upload accounting documents (certificates, conclusions);
- maintain the proficiency testing scheme database with full information about the proficiency testing round, participant, proficiency test item, etc.

In accordance with the provider's quality management system, the responsible employee checks the correctness of calculations and the performance of this SOFTWARE on a quarterly basis.



Показатель/характеристика: Жесткость общая
Тип результатов: Коли…
Ед. изм.: °Ж
Кол-во репликаций: 1
Метод определения приписанного значения: Согл…
Станд. откл. для оценки квалификации σ pt: По ре…
Допустимая погр. δE:
Приписанное значение x pt (ПЗ): 4.276
Неопределенность ПЗ u(x pt): 0.024
Станд. откл. σ pt:
Ориент. значение:

Уча…	Код	Дан…	x1	x	r	…	σ pt	D	D%	z	z'	Pa	En	ζ	…	Методика
…	A190	11-38	4.28	4.28			0.3…	0.004	0.0…	0.0…	0.0…				16	ГОСТ 31954-2012
Лаб…	A192	11-56	4.08	4.08			0.3…	-0.…	-4.…	-0.…	-0.…				3	ГОСТ 31954-2012
ФГБ…	A200	11-76	4.30	4.30			0.3…	0.024	0.5…	0.0…	0.0…				…	ГОСТ 31954-2012
ГУП …	A034	11-80	4.78	4.78 (не вып. 3.2516 …			0.3…	0.504	11.…	1.5…	1.5…				34	ГОСТ 31954-2012

Простые оценки

Среднее арифметическое: x* 4.2873
Медиана: x* 4.295
Стандартное отклонение: s* 0.0918 u(x) 0.0209
MADe: s* 0.0815 u(x) 0.0186
nIQR: s* 0.0815 u(x) 0.0186

Алгоритм А

Алгоритм А с итерат. шкалой: x* 4.283825280
Алгоритм А с итерат. шкалой: s* 0.085 u(x) 0.019

Сложные оценки

Метод Хампеля 1 (MADe): x* 4.2830672048456
Метод Хампеля 1 (Qn): x* 4.2826116900302
Метод Хампеля 1 (Q): x* 4.2843308412812
Метод Хампеля 2 (Q): x* 4.2873000000000
Qn метод: s* 0.0790 u(x) 0.0180
Q метод: s* 0.0876 u(x) 0.0200

☐ Включить выбросы при расчете робастных оценок
Уровень значимости для определения выбросов: 5%
Детализация графиков: 7
Граница зоны действия: 3
☑ Авторасчет среднего

Fig 2. Example UniLIMS

With all its advantages, no SOFTWARE can replace the coordinator of proficiency testing provider, because it is the coordinator:

- creates reference lists of proficiency test item, indicators, methods, units of measurement, participant (name, certificate, address) etc;
- fills in the system (participant, indicators, object, units of measurement, test results, etc.);
- analyzes the data received from the participants, on the basis of which:
- decides on the most appropriate method for calculating the assigned value and standard deviation for proficiency assessment);
- selects the criteria for evaluating laboratory performance and the method for calculating laboratory performance statistics;

- interacts with participants, etc.

It is with effective interaction of the Provider's employees with software, that it is possible to maintain a high level of quality of the proficiency testing scheme and implement the Provider's quality policy.

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METROLOGICAL SUPPORT OF NUCLEIC ACIDS MEASUREMENTS

Maxim S. Vonsky, Andrey L. Runov, Yurij A. Kustikov

D.I. Mendeleev Institute for Metrology, Saint Petersburg, Russia
ORCID ID 0000-0003-4061-7411, m.s.vonsky@vniim.ru

Keywords: nucleic acids; sequence; copy number; reference material; DNA amplification; target sequence; digital polymerase chain reaction

Deoxyribonucleic acid (DNA) is a linear double-stranded polymer composed of four nucleotides - adenine (A), guanine (G), thymine (T) and cytosine (C). The double strand is stabilized by hydrogen bonds according to the complementarity principle - bonds are formed between nucleotides A and T or C and G, located on different strands. Mutual position of nucleotides in the DNA chain, their sequence, is a nominal property, the material carrier of which is a DNA fragment containing the corresponding specific sequence. Sequence is a unique feature, a specific biomarker, identification of which makes it possible to unambiguously determine presence of the target DNA. The most well-characterized sequences of genomes of various organisms constitute the database of reference sequences RefSeq (https://www.ncbi.nlm.nih.gov/refseq/). Currently, RefSeq considered as the highest level of metrological traceability in the analysis of nucleotide sequences: it is common to publish sequencing results with reference to the sequence in RefSeq, indicating the identified differences. The uniqueness of the sequences, the availability of information on reference sequences determines the widespread use of the nucleic acids analysis methods in laboratory medicine, forensic medicine, biopharmaceutical industries, veterinary research, food and feed control. Examination of nominal properties, identification of target sequences a practically performed by means of polymerase chain reaction (PCR) with end-point detection.

Measurements of target sequences content are usually performed by real-time, or quantitative PCR (qPCR) method. qPCR is a relative method, content of the target fragments is determined in relation to the calibrator / reference material. In case of qPCR, the DNA content in reference materials is expressed as a mass fraction (g/kg) or as a percentage, and in some cases, for example, in WHO reference materials, - in international units (IU).

Measurements performed by qPCR applications are very sensitive to DNA purity and differences in template DNA content. Presence of the thermostable DNA polymerase inhibitors, as well as the high GC content of template DNA, affects the amplification efficiency and leads to significant systematic errors in the results of measurements.

Direct measurement of the target DNA sequences content, without relations to calibrators, became possible after development and implementation of the digital PCR (dPCR) method. Implementation of this method involves the direct recalculation of numbers of thousands microreaction volumes, in which fluorescent signal depends on occurrence of the PCR reaction. Further calculations of the target DNA molecules number are carried out using the Poisson distribution. A distinctive feature of this method is its reduced susceptibility to differences in amplification efficiencies and the presence of inhibitor impurities in the sample DNA solution, as well as a higher sensitivity compared to qPCR. The dPCR is an absolute method and does not require the use of any reference materials or calibrators for its implementation, while results of measurements of target DNA fragments number, i.e. number of DNA fragments formed by a certain sequence of nucleotides are expressed in units of "copy number per microliter" (cp/μl). According to the 9th edition of the "International System of Units SI" brochure (BIPM), the number of copies of a particular nucleic acid sequence refers to quantities that cannot be expressed in terms of seven basic SI units, but can be calculated, such as number of molecules, number of cellular or biomolecular objects. Calculated quantities are also quantities with the unit "one". The unit "one" is a neutral element of any system of units - it is necessary and is included in any system of units automatically. Thus, the formal traceability of the copy number to SI is established using appropriate validated measurement techniques [1].

A number of international pilot and key comparisons at the highest level of accuracy carried out by the Working Group on Nucleic Acid Analysis under the auspices of the Consultative Committee on Quantity of Substance (Analytical Chemistry and Biology) (CCQM) demonstrated, that application of dPCR ensures obtaining comparable results of target sequences content measurements in the range close to the limit of quantitative measurements of DNA - about 10 cp/μl and in the ratio of the target sequences number of copies up to 1: 1000 (0.1%).

Results of the VNIIM successful participation in international key comparisons CCQM-K86c [2] was used to support our CMC claim in the field of DNA measurements. The first string on DNA measurements capabilities for the Russian Federation was registered in the BIPM CMCs Database in 2019. Recognition of this measurement capability allows us to ensure traceability of nucleic acid measurements to the copy number as a non-systemic SI unit. Transfer of DNA content units from NMI can be implemented through certification of internal reference materials of enterprises - manufacturers of qPCR kits to the equipment they use and then - through transferring a unit to calibrators included in the kits applied by end users. In addition, it is possible to transfer units directly from the NMI to end-user laboratories through appropriate DNA reference materials of approved type.

At present, NIST (USA), NIBSC (Great Britain), JRC (EU) and NIM (China) are the leaders in the production of DNA CRMs certified by the number of copies. A large number of DNA CRMs intended for laboratory medicine applications is produced under the auspices of the WHO, however, the certified values of the DNA content in these CRMs are expressed in international units (IU). The only available DNA CRM of the approved type in the Russian Federation today is CRM of soybean DNA composition GSO 9866-2011 (set GM-soy-VNIIM), designed for verification of equipment for real-time PCR. The development and approval of the type of a standard sample of the human DNA composition is nearing completion: the certified values of this reference material is metrologically traceable to the State Ethalon GET 208 in terms of the mass (molar) fraction of the target sequences content, and to SRM 2372a NIST - in terms of the copy number content.

In the coming years we are planning to develop a number of DNA CRMs - biomarkers of infectious agents, including matrix CRMs, allowing to take into account influence of the biological material matrix on the sample preparation procedure, as well as the creation of CRMs for the needs of the biopharmaceutical industry and laboratory medicine, which will make it possible to proclaim formation of a system of metrological support for nucleic acids measurements.

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DEVELOPMENT OF REFERENCE MATERIALS FOR OPTICAL NANOSENSOR SYSTEMS

Anna A. Yushina, Michael K. Alenichev

All-Russian Scientific Research Institute for Optical and Physical Measurements, Moscow, Russia
e-mail: vniiofi@vniiofi.ru

Keywords: reference material, optical nanosensor system, disease marker, food contaminant, quantum dots, nanoparticles, dynamic light scattering, fluorescence

In recent years, the development of optical nanosensor systems has been actively progressing, due to the unique optical properties of nanosized particles allow highly sensitive detection of chemicals, microorganisms and biological molecules, including chemical contaminants of food products and the environment, as well as disease markers [1]. In many cases, such systems allow express analysis to be performed directly at the point of sample collection (point of care diagnostics). The basis for optical nanosensors is the measurement of absorption, fluorescence, or light scattering by nanoparticles that interact with the analyte [2].

Optical nanosensor systems based on dynamic light scattering (DLS) and fluorescence have been developed at VNIIOFI.

DLS-based nanosensors are designed to detect antibodies to *Aspergillus galactomannan*, a marker of a dangerous fungal infection of aspergillosis, and to analyze two food contaminants – the antibiotic chloramphenicol [3] and the mold fungus *Aspergillus*.

The operation concept of the system for determining the mold fungus *Aspergillus* is as follows:

1) antibodies to *Aspergillus galactomannan* are immobilized on the surface of gold nanoparticles to form conjugates which aggregate after being introduced into the analyte solution;

2) DLS measurements record an increase in the hydrodynamic diameter of nanoparticles;

3) the concentration of the analyte is determined using a calibration curve.

The operation of optical systems for the determination of food contaminants is based on competitive immunoassay using two types of gold nanoparticles conjugates functionalized with the analyte and antibodies to it, respectively:

1) the analyzed sample is mixed with a solution of nanoparticles functionalized with analyte molecules, followed by incubation of the mixture with a nanoparticle-antibody conjugates;

2) a decrease in the aggregation of functionalized nanoparticles leads to a decrease in the average hydrodynamic diameter of nanoparticles, determined by the DLS method;

3) the concentration of analyte in the sample is determined using a calibration curve.

The fluorescent nanosensor systems developed at VNIIOFI are based on the specific properties of quantum dots and designed for the detection and quantitative determination of reduced glutathione, a marker of ischemic stroke and a number of other diseases. Operational principle of one of the systems is based on the fluorescence resonance energy transfer (FRET) of ligand-functionalized quantum dots to another fluorophore, while the excitation spectrum of the acceptor overlaps with the emission spectrum of the donor. The presence or absence of reduced glutathione in this system affects the efficiency of energy transfer between the donor and acceptor due to the interaction of reduced glutathione with ligands. As a result, there is a change in the distance between them, which leads to characteristic changes in the fluorescence intensity in the emission spectra.

Operational principle of another fluorescent nanosensor is to turn off fluorescence under the influence of an acceptor that does not have fluorescent properties, followed by its recovery when reduced glutathione is added to the system (the effect of transferring excitation energy of quantum dots). The dependence of quantum dots restored fluorescence intensity on the concentration of the added reduced glutathione allows one to construct a calibration curve for determining reduced glutathione in an unknown sample.

Currently, a nanosensor system using silver nanoparticles, which will allow the determination of reduced glutathione by the surface enhanced Raman scattering (SERS), is being developed.

Also, the methods for measuring the mass concentrations of disease markers, reduced glutathione and antibodies to fungal infection, using optical nanosensor systems based on DLS and fluorescence, and methods for measuring the mass concentrations of food contaminants (chloramphenicol and Aspergillus fungus) using optical nanosensor systems based on DLS were developed.

All nanosensor systems described above require the construction of calibration curves, which needs reference materials of the corresponding analytes. In order to provide metrological support for measurements carried out using optical nanosensor systems developed at VNIIOFI, reference materials that allow reproducing mass concentrations of reduced glutathione and chloramphenicol were developed. For these reference materials, the category "enterprise reference material" was selected, in accordance with the terminology of GOST 8.315-2019 [4].

To reproduce the mass concentration of reduced glutathione, it was considered expedient to develop a reference material for the mass fraction of this substance, which allows preparing calibration standards reproducing mass concentrations in a wide range of values.

Enterprise reference material of reduced glutathione is a powder with an analyte mass fraction of ~98% and is intended for preparation of calibration standards immediately before use; deionized water is recommended as a solvent.

Standardized metrological characteristics of the enterprise reference material of reduced glutathione are the mass fraction of reduced glutathione in the enterprise reference material (%) and the value of the extended uncertainty of the certified value at the coverage coefficient k = 2.

To reproduce the mass concentration of chloramphenicol, an alcohol-based reference material was developed. Enterprise reference material of chloramphenicol is an ethanol solution with a mass concentration of chloramphenicol of ~1 g/dm^3, it is supposed to be diluted to prepare calibration standards immediately before use.

Standardized metrological characteristics of the enterprise reference material of chloramphenicol are the mass concentration of chloramphenicol in the enterprise reference material (g/dm^3) and the value of the extended uncertainty of the certified value at the coverage coefficient k = 2.

The developed enterprise reference materials are intended for metrological support of methods for measuring chloramphenicol and reduced glutathione using optical nanosensor systems developed at VNIIOFI.

It should be noted that the developed enterprise reference materials can also be used for verification and calibration of the "point of care diagnostics" type compact detection devices being developed, which can be used for express analysis directly at the sample collection point.

The values of the standardized metrological characteristics of the developed enterprise reference materials are shown in table 1.

Table 1. Metrological characteristics of enterprise reference materials

Name of the characteristic	**Range of acceptable certified values**	**The expanded uncertainty of certified value at k = 2, %**
Mass fraction of reduced glutathione, %	98,0 – 100,0	± 1

Mass concentration of chloramphenicol, g/dm^3	9,5 – 10,5	± 5

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USAGE OF STANDARD MATERIALS OF ABSORBED DOSE FOR VALIDATION OF A STERILIZATION PROCESS FOR MEDICAL DEVICES AND FOOD PROCESSING

Alexandr P. Zhanzhora, Oleg I. Kovalenko, Alexandr A. Gromov

All-Russian Scientific Research Institute of Physical Technical and Radio Technical Measurements
Moscow region, Mendeleevo, Russia
e-mail: zhanzhora@vniifnri.ru

Keywords: standard materials, absorbed dose, radiation treatment, ionizing radiation, food products

Radiation sterilization of medical devices, radiation treatment of food and agricultural products are industrial technological processes related to the treatment of these products with ionizing radiation. Products are processed at specialized radiation processing plants, mainly using electron accelerators. When carried out correctly, these processes are safe and reliable.

Since any radiation technological process is a special process, the results of which cannot be fully checked by subsequent non-destructive testing of products, it is subject to validation.

Process validation is a documented procedure for obtaining, recording, and interpreting results, which is necessary to confirm that the output of the process will be reproducible and produce products that meet pre-defined technical requirements.

When validating these processes, much attention should be paid to the certification of installed equipment and certification of the radiation processing plant for the absorbed dose in the irradiated objects, which is carried out when putting products into production after testing the processing technology of these products.

When carrying out verification of the installed equipment it is established that:

- the electron energy does not exceed 10 MeV;
- the uneven distribution of the electron beam current density along the output window of the accelerator does not exceed 10%;
- the instability of movement of irradiated objects in the irradiation zone does not exceed 5%;

When verifying a radiation processing plant for the absorbed dose in products with electron accelerators, the following parameters are set:

- possibility of irradiation of objects in the set range of absorbed doses;
- range of absorbed doses at the control point;
- proportionality coefficients Kmin and Kmax, which determine the relationship between the dose at the reference point and the minimum and maximum values of absorbed dose in products under regulated irradiation conditions;
- minimum, Vmin, and maximum, Vmax, speed of product movement under the electron beam.

The report will present the results obtained during the verification of the installed equipment and verification of the radiation processing plant for the absorbed dose in products with electron accelerators. Measurements during verification were carried out using an approved type of standard materials of the absorbed dose of СО ПД(Ф)Э-5/50, СО ПД(Ф)Р-5/50, СО ПД(Э)-1/10 developed and produced by VNIIFTRI.

ENSURING THE UNIFORMITY OF MEASUREMENTS IN THE FIELD OF LUMINESCENCE. STANDARD SAMPLE OF AN AQUEOUS SOLUTION OF ADENOSINTRIPHOSPHATE SODIUM

Irina N. Zyablikova, Alexander V. Ivanov, M.M. Chugunova, Anna N. Shobina

All-Russian Scientific Research Institute for Optical and Physical Measurements, Moscow, Russia
e-mail: vniiofi@vniiofi.ru

Key words: state standard sample, adenozintrifosfat sodium (ATP) luminescence.

Improving the quality of products, improving their consumer properties and extending the shelf life is what food manufacturers strive for. A necessary condition for achieving these goals is a high level of sanitation and hygiene at all production sites and facilities of the enterprise. According to the requirements of Rospotrebnadzor, since February 2015, all companies and enterprises that are engaged in the production or packaging of food products must implement the HACCP quality management system (Hazard Analysis and Critical Control Points). This requirement is prescribed in the technical regulations of the Customs Union TR CU 021/2011 "on food safety". These quality management systems are used to ensure the safety of production processes, as well as to reduce the risks that may arise during the production and sale of food products.

Generally accepted methods for determining the degree of biological contamination of production surfaces, water and hands of personnel have a significant drawback – a long time to obtain results. According to HACCP requirements, after washing and disinfecting equipment in production, it is necessary to perform not only microbiological control, but also control of product residues. With this approach, the best approach is to use ATP-luminometry-a method of "rapid Microbiology". Table 1 shows a comparative analysis of the time of obtaining the results of the degree of biological contamination by various methods.

Table 1.

Diagnostic method	Time of getting the result
Microbiology real-time	6 – 30 hours
PCR real-time	1,5 hours
ATP-luminometry	15 seconds

The principle of operation of luminometers is based on the principle of bioluminescence. . This is the ability of living microorganisms to release light energy in the process of life and certain chemical reactions. All objects of animal and plant origin, including food particles, live and dead bacteria, fungi and other microorganisms contain a molecule of adenosine triphosphate (ATP). During the analysis, the reaction of the ATP molecule and the enzyme luciferin (luciferase) occurs, which results in a glow proportional to the amount of ATP available. By measuring the strength of this glow, you can determine the degree of biological contamination of the studied area. The greater the glow , the more microorganisms there are.

Luminometers measure the intensity of light emitted by a sample and display the test result in relative light units (RLU). Although relative light units are not a real physical measure of light intensity, they nevertheless allow an objective assessment of the bioluminescence intensity, depending on the concentration of ATP. So 1 RLU of bioluminescence, approximately, corresponds to 1 femtomol (10^{-15} mol) of ATP. This amount of intracellular ATP is contained in several microbial cells, which is equivalent to a single CFU on the nutrient medium. However, for different manufacturers of luminometers with the same level of surface contamination by microorganisms, the value in RLU may differ. Therefore, the metrological traceability of these devices is established using calibration graphs, in which the values of the bioluminescence intensity in RLU are linked to the concentration of the ATP solution.

In 2020, FSUE “VNIIOFI” developed a standard sample of sodium adenosine triphosphate solution as part of the task of facilitating the verification procedure and ensuring metrological traceability of luminometers in a unit of mass concentration. The standard sample is a solution of sodium adenosine triphosphate in distilled water, packaged in ampoules with a capacity of 5 and 10 cm^3. Certified characteristic: mass concentration of sodium adenosine triphosphate, g/dm3. The range of acceptable certified values of CO: 0.09-0.11 g / dm^3. The allowed value of the absolute extended uncertainty (with the coverage coefficient k=2) is 0.015 g/dm^3.

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UNIIM RESULTS OF PARTICIPATION IN A KEY COMPARISON OF COPPER CALIBRATION SOLUTIONS PREPARED BY NATIONAL METROLOGICAL INSTITUTES

Veniamin M. Zyskin, Pavel V. Migal, AlenaV. Sobina, Aleksandr Yu. Shimolin

UNIIM – Affiliated Branch of the D.I. Mendeleyev Institute for Metrology, Ekaterinburg, Russia
e-mail: zyskinvm@uniim.ru

Ural Research Institute for Metrology (currently UNIIM is a branch of the D.I. Mendeleev Institute for Metrology, hereinafter – UNIIM) in 2017-2020 took part in the key comparison CCQM-K143 "Comparison of copper calibration solutions prepared by national metrological institutes", coordinated by the National Institute of Standards and Technology (NIST), USA, in which national metrology institutes from 19 countries participated.

Each participant of comparisons, according to the Technical Protocol, had to prepare a nitric acid solution with a given value of the mass fraction of copper in the range from 9.9 g/kg to 10.1 g/kg and a mass fraction of nitric acid from 6 % to 8 % using their own source materials, submitting the protocol of solution preparation to the coordinator of the comparison. The copper mass fraction and the corresponding expanded uncertainty were to be established by the participant from his own measurements.

The resulting solution should be dispensed into ten 60 ml HDPE bottles, each containing (25.0 ± 0.3) g of solution, weighed with discreteness of 0.1 mg, packed in aluminized polyester bags provided by NIST, and sent to the coordinator of the comparison.

The certified reference material (CRM) of the composition of high-purity copper (Cu CRM UNIIM) CRM 10800-2016, manufactured by UNIIM has been used as a source material for the preparation of a copper calibration solution in the framework of the CCQM-K143 key comparison. The metrological characteristics of this CRM were established by the primary method of controlled potential coulometry with using the state primary standard GET 176 (currently the State primary standard of units of mass (molar, atomic) fraction and mass (molar) concentration of components in liquid and solid substances and materials based on coulometry GET 176-2019) and are shown in Table 1.

Table 1.Metrological characteristics of CRM of high purity copper (Cu CRM UNIIM) CRM 10800-2016 (batch No. 1)

CRM number	CRM certified characteristic	CRM certified value, %	Expanded uncertainty of the certified value $U_{(k=2)}$, %	Limits of the absolute error of the certified value Δ, % (P=0,95)
10800-2016 (Cu RM UNIIM)	Mass fraction of copper	99,994	0,012	0,012

Measurements of the mass fraction of copper in the prepared calibration solution were carried out by two methods: the primary method of controlled potential coulometry (CPC) and the method of high-performance optical emission spectroscopy with inductively coupled plasma (HP-ICP-OES) relative to a solution of the high-purity copper reference standard RS-1.3-176-001-2016-Cu. The measurements were carried out twice: from the flask after preparation and from packaged bottles. In both cases, an increase in the measurement result was observed after packing the solution. The value of the mass fraction of copper in packaged bottles, obtained by the CPC method, was 10,0006 g/kg (an increase in the result by 0.0042 g/kg) by the HP-ICP-OES method was 9.9812 g/kg (an increase in the result by 0.0035 g/kg).

The mass fraction of copper in the calibration solution, calculated according to the preparation procedure, was 9.9910 g/kg.

The contributions due to the uncertainty of the source material, inhomogeneity between bottles, instability of solutions during storage, and characterization by two measurement methods (CCP and HP-ICP-OES) were taken into account, when compiling the uncertainty budget for the mass fraction of copper in the prepared solution. The relative expanded uncertainty was 0,18 % with a coverage factor of k = 2. The mass fraction of nitric acid in the prepared copper solution according to the titration results was 6,9 % with a relative expanded uncertainty of 0.4 % (k = 2), which corresponded to the requirements of the technical protocol of the comparison. The copper solution, packed in accordance with the requirements of the technical protocol, was sent to the coordinator (NIST).

Calibration solutions prepared by all participants were measured at NIST using high performance optical emission spectroscopy with inductively coupled plasma, and then the results were compared in relative scale without calibration. These results were confirmed by the second series of measurements by the ICP-OES method, carried out at the National Metrology Institute of Germany – PTB. The measurement results are shown in Figure 1.

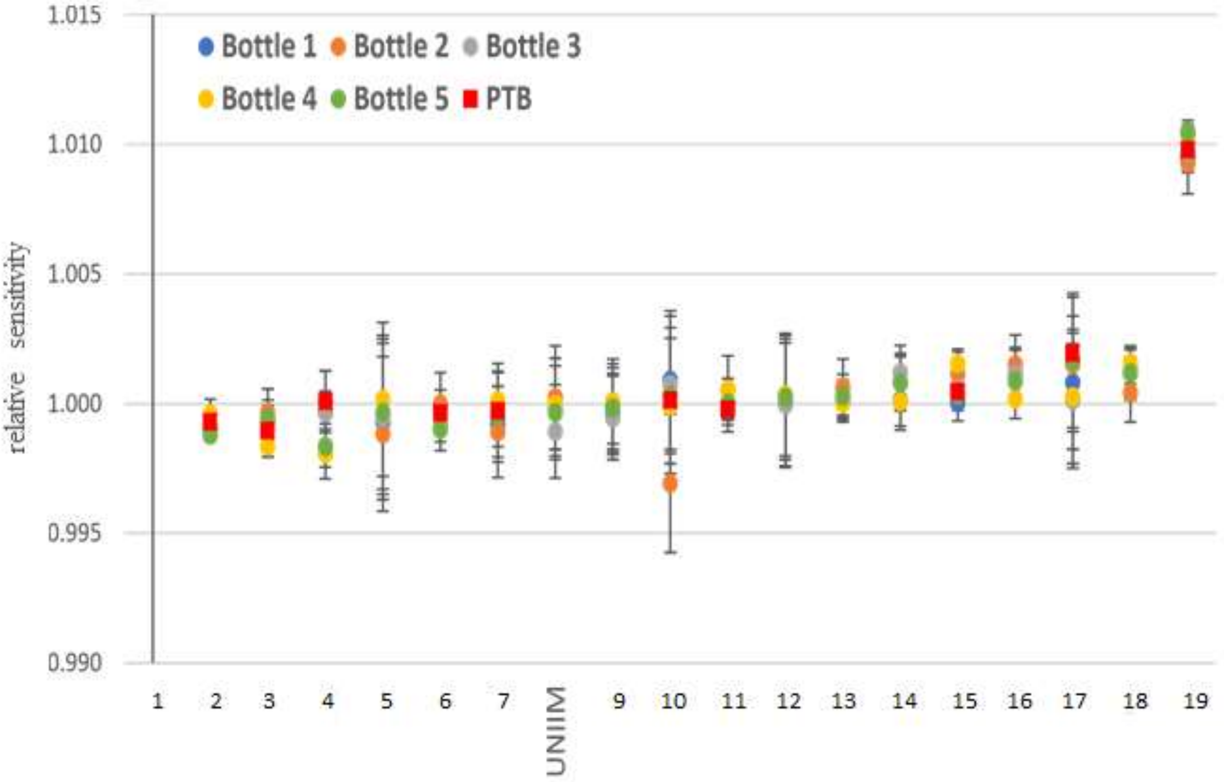

Fig. 1. NIST measurements in five bottles provided by each participant and PTB measurements in one bottle for a sample subset of participants (vertical bars represent expanded uncertainty, k = 2).

Measurements by NIST and PTB showed that the majority of participants performed equivalently. The values of the degree of equivalence are shown in Figure 2 (for the two participants it was impossible to compare the results due to calculation and preparation errors).

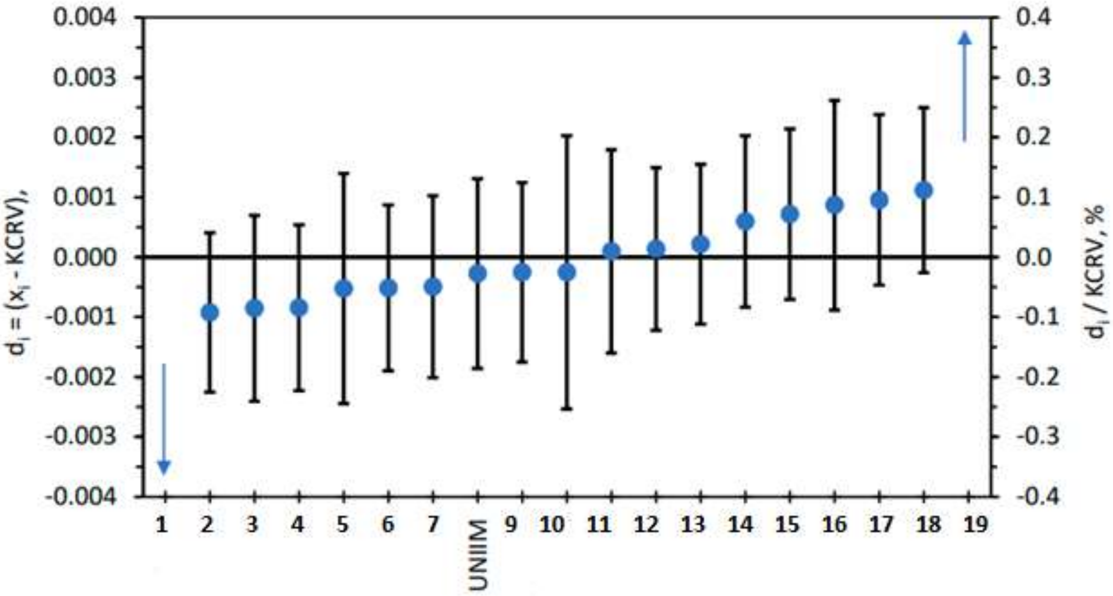

Fig. 2 Degrees of equivalence of participants (vertical bars correspond to expanded uncertainty, k = 2)

Thus, by successful participation in the CCQM-K143 key comparison, UNIIM confirmed the possibility of preparing reference materials of the composition of copper ions solutions with a relative expanded uncertainty of the certified value of 0,18 % (k = 2). According to the CCQM-K143 comparison report, successful participation confirms the competence in the preparation of not only copper solutions, but also solutions of other metals that can be relatively easily transferred into solution.

Alphabetical Index

CONFERENCE ABSTRACTS

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REFERENCE MATERIALS IN MEASUREMENT AND TECHNOLOGY

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4, Krasnoarmeyskaya St., Ekaterinburg, 620075, Russian Federation,
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