III МЕЖДУНАРОДНАЯ
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En

СТАНДАРТНЫЕ ОБРАЗЦЫ
В ИЗМЕРЕНИЯХ И ТЕХНОЛОГИЯХ

REFERENCE MATERIALS
IN MEASUREMENT AND TECHNOLOGY

Тезисы докладов
конференции

Conference
abstracts

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FEDERAL AGENCY ON TECHNICAL REGULATING AND METROLOGY
URAL RESEARCH INSTITUTE FOR METROLOGY
SCIENTIFIC METHODICAL CENTRE OF STATE SERVICE OF REFERENCE MATERIALS FOR COMPOSITION AND PROPERTIES OF SUBSTANCES AND MATERIALS

THIRD INTERNATIONAL SCIENTIFIC CONFERENCE

REFERENCE MATERIALS IN MEASUREMENT AND TECHNOLOGY

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The Conference proceedings contain materials on general theoretical, metrological and practical issues of the creation, application of reference materials. The materials provided by the authors are 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!
Welcome to the III International scientific conference
“Reference materials in measurement and technology”

The III International Scientific Conference “Reference materials in measurement and technology” (11-14 September, 2018) is held when in the focus of attention is the digital transformation of the economy, industry, social sphere and the whole quality infrastructure.

Measurement uniformity assurance should become one of the main instruments in the development of innovative directions of the digital economy, and therefore the informatization and digitalization of functioning of the system for measurement uniformity assurance is rapidly increasing.

Metrological activity in digital transformation is infrastructural and providing due to the receipt of complete, timely, reliable measurement results. This is especially important in the areas of health, pharmaceuticals, production and diagnostic equipment maintenance, provision of environmental safety and labor safety. The trend is toward measurement instruments with distributed, virtualized components and the use of ‘cloud’ services and databases.

Intelligent systems will simplify and optimize production, help in the development of new technologies, substances. Even now, new technologies allow getting more and more accurate data about objects of measurements, data processing technologies help to develop new, improved approaches and algorithms for analyzing the received measurement data. All this will allow getting more accurate data for experimental research in the development of reference materials. At the same time, these same aspects show the need for improving the nomenclature of reference materials, together with the increased requirements for the quality of reference materials.

The need to formulate proposals for improving legislation and developing the necessary solutions in this area has arisen. These are the first steps aimed at developing digital technologies and electronic registration of the main results of metrological works.

Within the framework of digitalization, one of the main problems is the improvement of the system for collecting, processing, storing and distributing data. The rapid development of integration processes, and also the need to increase the level of availability of reference materials to Russian consumers, raises the question of optimizing the mechanisms and methodology of research and forecasting the needs of the government and society in metrological support of measurements, including by applying reference materials, increasing competitiveness and recognizing reference materials on the international market. The main tasks of metrological support are monitoring and prompt response to the growing demands of industry and the economy in the framework of the global digitalization. This explains why in the Strategy for measurement uniformity assurance of the Russian Federation until 2025 approved by the decree of the government, a significant role is given to issues in the field of RMs and the creation of necessary nomenclature of RMs.

Leading specialists in the field of measurements and reference materials from different countries are working on solving these and other issues. They are being discussed at meetings of international metrology organizations, at international and regional conferences.

The III International Scientific Conference ‘Reference Materials in Measurement and Technology’, uniting manufacturers and consumers of reference materials from different countries, is aimed at discussing topical issues in the field of creating, applying reference materials in order to ensure accuracy, uniformity and comparability of measurements.

Organizers of the III International Scientific Conference
“Reference materials in Measurement and Technology”
wish the conference participants active and fruitful work,
establishment of new contacts for the formation of new promising projects!

CONTENTS

STATE REGISTER OF APPROVED TYPE REFERENCE MATERIALS OF THE RUSSIAN FEDERATION

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State Register of reference materials of approved type (State Register of approved type reference materials for composition and properties of substances and materials, State Register of RMs) is a control and accounting element of the State Service for Reference Materials of Composition and Properties of Substances and Materials and is intended for registration of reference materials which types were approved under the established procedure by the Federal Agency on Technical Regulating and Metrology (Rosstandart).

Rosstandart decides on type approval of the reference material (in the form of an order) based on the test results of the reference material.

State Register of RMs consists of the following parts:

- reference materials, which types are approved by Rosstandart;
- document fund for reference materials of approved type.

The Scientific Methodical Centre of the State Service for Reference Materials of Composition and Properties of Substances and Materials (Ural Research Institute for Metrology) is responsible for maintenance of the State Register of RMs.

Aims of the State Register of RMs:

- registration and recording of reference materials of approved type;
- development of a central fund of data on reference materials of approved type;
- development of a central fund of documents on development, tests and approval of reference materials which were admitted to production and use in the Russian Federation;
- registration and recording of issued certificates for type approval of reference materials;
- informational services for interested parties (legal bodies and private persons) including participants of State Service for Reference Materials of Composition and Properties of Substances and Materials.

One of the main functions of the State Service for Reference Materials of Composition and Properties of Substances and Materials is the informational support in the field of reference materials – meeting the needs in the following spheres: information support of some development and activity programs of the State Service for Reference Materials of Composition and Properties of Substances and Materials, scientific research, development of reference materials, their production, metrological supervision over their use, and cooperation programs in the field of reference materials.

In order to ensure accessibility of information on reference materials used in the sphere of state regulation of measurement uniformity assurance, Rosstandart created the Federal Information Fund for Ensuring the Uniformity of Measurements, one section of which includes “Data on reference materials of approved type” [https://fgis.gost.ru/fundmt/], which is based on the data from State Register of reference materials of approved type and includes the following information: RM name; number of RM in the State Register; number of certificate of type approval; certificate validity

period; RM description; country, RM producer; certified characteristic of RM; way of establishing RM certified value.

Issues of the informational service development in the field of reference materials are priority orientations of the activities of the State Service for Reference Materials of Composition and Properties of Substances and Materials, and the State Register of RMs is a tool in resolving them.

ESTIMATION OF CONSENSUS VALUE OF INTERLABORATORY MEASUREMENT RESULTS WITH MINIMUM INCREASE OF ASSOCIATED UNCERTAINTY

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The use of interlaboratory experiment in characterization of reference materials and other tasks of metrology lead to the necessity of estimating the consensus value of the measurand from measurement results $\{x_i, u_i\}$, $i=\overline{1,n}$ (measurement result and its standard uncertainty), obtained in n independent laboratories. The standard estimate of the measurand is the weighted mean

$$\overline{x}_0 = u_0^2 \sum_{i=1}^{n} u_i^{-2} x_i \quad , (1)$$

where u_0^2 is the square of the standard uncertainty (variance) of the estimate

$$u_0^2 = \left(\sum_{i=1}^{n} u_i^{-2} \right)^{-1} \quad , (2)$$

Such an estimate is applied, when the data $\{x_i, u_i\}$ with $i=\overline{1,n}$ are consistent, i.e., with high probability P the condition is satisfied

$$\sum_{i=1}^{n} \frac{(x_i - \overline{x}_0)^2}{u_i^2} \le \chi^2(P; n-1) \quad , (3)$$

where $\chi^2(P; n-1)$ is P–quantile chi-square of the distribution with (n-1) degrees of freedom. If condition (3) is not satisfied, the data are considered as inconsistent, i.e., measurement results contain systematic errors, not included in uncertainties, stated by laboratories.

Data inconsistency, i.e. the dispersion of measurement results x_i between laboratories is often described by normal distribution centered in the target value of the measurand and interlaboratory variance σ2, which characterizes the inconsistency of the measurement results. In this case, to make the data consistent, the standard uncertainties of each laboratory are increased from u_i^2 to $u_i^2 + \sigma^2$, ($i=\overline{1,n}$) and the weighted mean $\overline{x}_\sigma$ and its variance u_σ^2 are calculated by formula (1) with the new weights. The methods of estimating the parameter σ2 are known [1 1]. After the uncertainties of the measurement results of the laboratories are increased by this way, the data become consistent, i.e., they meet criterion (3).

An obvious weakness of this approach is not always a justified increase of the uncertainties of measurement results of all laboratories and, as a consequence, an increase of the uncertainty of the target estimation of the measurand. In this paper, we propose a more economical way with respect to increasing uncertainty to make data consistent by selecting a part of measurement results which are already consistent and it is not necessary to increase their uncertainty.

Let’s make use of the scheme, proposed in [2 2]. If the condition of consistency (3) for n laboratories is not satisfied, we’ll order the pairs of data $\{x_i, u_i\}$ ($i=\overline{1,n}$) in such a way, that

$$\frac{(x_1-\overline{x}_0)^2}{u_1^2} < \frac{(x_2-\overline{x}_0)^2}{u_2^2} <\ldots< \frac{(x_n-\overline{x}_0)^2}{u_n^2} \quad , (4)$$

Let’s reject the data of a laboratory with number n and recalculate the estimates (2) and shi-square statistics from condition (3) for (n-1) laboratories. We’ll repeat the process until the condition of consistency is not satisfied for some k.

$$\sum_{i=1}^{k}\frac{(x_i-\overline{x}_k)^2}{u_i^2} \le \chi^2(P;k-1) \quad , (5)$$

$$\overline{x}_k=\left(\sum_{i=1}^{k}u_i^{-2}\right)^{-1}\sum_{i=1}^{k}u_i^{-2}x_i \quad , (6)$$

где

Thus, we have selected the maximum set of consistent data k = 2, .., n in size. Let’s consider the parametric family of statistics

$$\overline{x}_\lambda=u_\lambda^2\left(\sum_{i=1}^{k}u_i^{-2}x_i+\sum_{i=k+1}^{n}\left(u_i^2+\lambda\right)^{-1}x_i\right) \quad , (7)$$

$$u_\lambda^2=\left(\sum_{i=1}^{k}u_i^{-2}+\sum_{i=k+1}^{n}\left(u_i^2+\lambda\right)^{-1}\right)^{-1} \quad , (8)$$

where

$$g(\lambda)=\sum_{i=1}^{k}\frac{(x_i-\overline{x}_\lambda)^2}{u_i^2}+\sum_{i=k+1}^{n}\frac{(x_i-\overline{x}_\lambda)^2}{u_i^2+\lambda} \quad , (9)$$

and

where the parameter λ specifies the increase of the variances in the inconsistent part of the data. With a proper choice of λ parameter value formula (7) is the estimate of the measurand and its variance, formula (9) is chi-square statistic constructed with regard to variance increase of an inconsistent part of data. In the assumption, that the dispersion of measurement results in an inconsistent part of data is described by a normal distribution with variance σ2, the statistic (9) with the parameter value λ = σ2 has chi-square distribution with (n-1) degrees of freedom and mathematical expectation equal to (n-1). That is the reason why we can choose λ parameter value λ from the equation

$$g(\lambda)=n-1 \quad , (10)$$

It is easy to show, that function $g(\lambda)$ decreases monotonically and

$$\lim_{\lambda\to\infty}g(\lambda)=\sum_{i=1}^{k}\frac{(x_i-\overline{x}_k)^2}{u_i^2} \quad , (11)$$

Hence, taking into account (5), it follows, that equation (10) has a solution if and only if

$$\chi^2(P;k-1)<n-1 \quad , (12)$$

This solution can be easily found numerically, it is a statistical estimate of the interlaboratory variance σ2. If the condition (12) is not satisfied and equation (10) has no solution, then the needed value λ can be found from inequality

$$g(\lambda)\le\chi^2(P;n-1) \quad , (13)$$

which always has a solution, since inf $g(\lambda) \leq \chi^2(P;k-1) < \chi^2(P;n-1)$ with k<n.

Thus, the proposed procedure with the consistent data (k = n) gives the standard solution (1), with inconsistent data (1 <k <n) guarantees by construction a smaller uncertainty than the methods recommended in [1] and only in the absence of an agreed set ($k \leq 1$) is equivalent to them (coincides with Mandel-Powell estimate).

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INTERNATIONAL COOPERATION IN THE FIELD OF REFERENCE MATERIALS FOR LABORATORY MEDICINE

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Keywords: reference material, bioassay, laboratory medicine, calibrator, control material, traceability, measurement standard, analyte, measurement unit

The construction of a metrological support system in the field of laboratory medicine is of great importance for the provision of quality medical services. Taking into account the wide variety of research methods used in laboratory medicine, including the use of different methods for measuring the same bioassay parameter, the creation of reference materials becomes particularly important. The use of reference materials for metrological support in the field of laboratory medicine makes it possible to determine the concentration of components in bioassays at a high level of accuracy, and also provides an objective tool for monitoring the quality of laboratory research conducted in analytical laboratories. Currently, the international metrology community pays special attention to ensuring the traceability of measurement results to national measurement standards or units of the International System of Units (SI).

In June 2002, the Joint Committee on Traceability in Laboratory Medicine (JCTLM) was established. JCTLM is formed by the International Bureau of Weights and Measures (BIPM), the International Federation of Clinical Chemistry and Laboratory Medicine (IFCC) and the International Laboratory Accreditation Organization (ILAC). The main objective of JCTLM is to ensure the implementation of the requirements of Directive 98/79 / EC (IN-VITRO-diagnostics). The main task of this committee is to ensure, at the international level, the reliability and equivalence of measurement results in the field of laboratory medicine, including the promotion of the concept of the need for traceability with SI units or other internationally recognized. Currently, JCTLM employs 35 organizations from 23 countries, including from the Russian Federation: VNIIM im. D. I. Mendeleev (St. Petersburg), VNIIMS (Moscow), VNIIOFI (Moscow).

To carry out their JCTLM mission, databases of reference materials, reference methods / procedures and reference measurement services in the field of laboratory medicine are organized and maintained.

The reference materials database includes reference materials that meet the requirements of ISO 15194: 2003 (GOST R 15194-2013, In vitro diagnostic medical devices -- Measurement of quantities in samples of biological origin -- Requirements for certified reference materials and the content of supporting documentation). In addition to the reference materials traceable to SI units (List 1), the JCTLM database also contains reference materials that are not traceable to SI units, but recognized by international agreements (List 2). As of July 2018, there are 293 reference materials in the database (the main contribution is USA-48 %, EU-21 %, Japan -13 %, Great Britain -8 %, other countries: France, Brazil, China, Singapore, Australia, Mexico from 1 to 4%). Also in the field of laboratory medicine, calibrators and control materials are applied, the requirements to which are defined in the standard ISO 17511: 2003 (GOST R 17511-2011, In vitro diagnostic medical devices. Measurements in biological samples. Metrological traceability of values assigned to calibrators and control materials).

The JCTLM database for reference methods / procedures is formed from methods that meet the requirements of ISO 15193:2009 (GOST R 15193-2015, In vitro diagnostic medical devices -- Measurement of quantities in samples of biological origin -- Requirements for content and presentation of reference measurement procedures). The database contains 184 reference procedures.

The database of reference metrological services includes a list of measurements performed by laboratories that meet the requirements of ISO 15195:2003 (GOST R 15195-2006, Laboratory Medicine, Requirements for reference measurement laboratories). The database contains 161 measuring services for various analytes in various bioassay matrices (the main contribution is Germany - 39%, China - 33 %, Great Britain - 7 %, other countries Japan, Belgium, France, Spain, Italy from 4 to 6 %).

JCTLM developed the document WG-2-P-00 “Hierarchical scheme for calibration and measurement in the field of laboratory medicine. Quality policy and definitions”, which defines the basic principles for national traceability systems in measurements:

- development and maintenance of national (mainly primary) measurement standards as the basis for traceability within the country;
- ensuring international equivalence of these measurement standards;
- the spread of traceability to the level of working capital.

International comparisons are the main element of interstate recognition of measurement and calibration capabilities. The International Bureau for Weights and Measures (BIPM) has conducted comparisons on the following analytes:

- Calcium in human serum (2003);
- Creatinine in human serum (2005);
- Glucose in human serum (2005);
- Nonpeptidic hormones in human serum (cortisol) (2007);
- Nonpeptidic hormones in human serum (progesterone) (2007);
- Quantitative PCR (2007);
- Steroid anabolics in urine (testosterone) (2008);
- Creatinine in human serum (2010);
- Relative quantitative evaluation of fragments of genomic DNA isolated from biological tissue (2010);
- Creatinine in human serum (2012);
- Glucose in human serum (2012);
- Cholesterol in human serum (2012);
- Elements and selenium in human serum (2013);
- Determination of purity of the peptide - synthetic peptide of human C (HCP) (2014).

International comparisons are planned for the following analytes: serum fecal and urea and uric acid in human serum.

For today the share of domestic reference materials for laboratory medicine is not great in comparison with foreign reference materials. The Federal Information Foundation for Ensuring Uniform Measurement contains 24 types of reference materials:

GSO 9104-2008 is a standard sample of blood composition containing lead (Pb (50-300 μg/dm3);

GSO 9056-2008 - a reference material for composition of blood serum SKCH-1;

GSO 9057-2008 - a reference material for composition of serum of blood SKCH-2;

GSO 9279-2008 - a reference material of a solution of glucose and lactate (RGL-1);
GSO 9280-2008 - a reference material of a solution of glucose and lactate (RGL-2);
GSO 9281-2008 - a reference material of a solution of glucose and lactate (RGL-3);
GSO 9624-2010 - a reference material for composition of blood cells - hematological control (HbA 95-160 g/l, Erythrocytes 2.0-5.5 * 1012 / L, counting concentration of leukocytes 2.5-9.0 * 1012 / L);
GSO 9653-2010 - a reference material for composition of blood containing mercury (Hg 4-40 μg/dm^3);
GSO 9866-2011 - a reference material of DNA SOI;
GSO 9913-2011 - a reference material of the molar concentration of cholesterol in the blood;
GSO 10023-2001 - a reference material of artificial urine;
GSO 10128-2012 is a reference material of blood composition containing cadmium, (Bl-Cd);
GSO 10129-2012 is a reference material of blood composition containing beryllium, (Bl-Be);
GSO 10157-2012 is a reference material of a fragment of the plasmid pUC18, consisting of 717 base pairs;
GSO 10167-2012 is a reference material of the mass concentration of class G immunoglobulins against the rubella virus in serum, human blood plasma (REDUC-lgG-LSA);
GSO 10236-2013 - a reference material of the composition of blood containing thallium, (Bl-TL)
GSO 10237-2013 is a reference material of the mass concentration of class G immunoglobulins to the TREPONEMA PALLIDUM bacterium in serum, human plasma (TREPONEMA PALLIDUM-IgG);
GSO 10238-2013 - a reference material of the composition of hemoglobin cyanide;
GSO 10280-2013 is a reference material of the mass concentration of the HBsAg antigen of the hepatitis virus in serum, human plasma (HBsAg HBV);
GSO 10281-2013 - a reference material of the mass concentration of the antigen p24 of the human immunodeficiency virus of the first type in serum, human plasma (p24 HIV-1);
GSO 10390-2013 - a reference material of the molar concentration of testosterone in the blood serum (Testosteron-VNIIM kit);
GSO 10669-2015 - a reference material of the composition of blood elements - hematological control (set GC-VNIIM);
GSO 10818-2016 is a reference material of the mass fraction of the amyloid-beta peptide monomer (mAβ42);
GSO 10920-2017 - a reference material of mass concentration of recombinant toxin CLOSTRIDIUM DIFFICILE in physiological buffer;
GSO 10921-2017 - a reference material of the mass concentration of the recombinant GP protein of the Ebola virus in phosphate-saline solution;
GSO 10922-2017 is reference material of the mass concentration of the recombinant protective antigen BACILILUS ANTHRACIS in phosphate salt solution.

To enhance the role of Russia at the international level in the field of laboratory medicine, it is necessary to develop a system of reference materials and reference procedures, establish their correspondence with international lists, incorporate into JCTLM databases, and accredit Russian analytical laboratories in accordance with JCTLM requirements.

INTERLABORATORY COMPARISON TESTS - THE MAIN TOOL OF COMPETENCE ASSESSMENT

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Keywords: interlaboratory comparison tests, competence assessment, metrology, measurement uniformity assurance, quantitative chemical analysis, provider, accreditation, reference material

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 No. 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:

- confirmation of competence of laboratories (centres) in the relevant field of activity;
- assessment of characteristics of the test method, as well as interlaboratory certification of the test procedure (measurements);
- assessment of characteristics of a reference material, as well as interlaboratory certification of the sample for control.

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 GSO (state reference material), IHRM (in-house reference material), as well as materials 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.

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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DEVELOPMENT OF INTERLABORATORY COMPARISON SAMPLES AND REFERENCE MATERIALS FOR THE QUALITY ASSURANCE OF AIR COMPOSITION MEASUREMENTS

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Keywords: interlaboratory comparison (ILC), ILC provider, ILC samples, reference materials, air media, atmospheric air, workplace air, industrial emissions to atmosphere, laboratory sample

In 2015, the interlaboratory comparison (ILC) provider Ural Research Institute for Metrology (UNIIM) for the first time conducted a series of ILC studies aimed at controlling the accuracy of hazardous substance measurements in various air environments, such as atmospheric air, workplace air and industrial emissions to the atmosphere. During the subsequent three years, the ILC of air environment measurements have attracted a large number of participants (laboratories), which is an evidence of a great demand for the external quality control of air composition measurements, as well as for the creation of ILC samples (samples for proficiency testing and control samples, hereafter referred to as samples) and respective reference materials (RMs).

The development of ILC samples for air environments is different from that for other objects (soil, water, food products, etc.), because in most cases (with respect to the measurement method used) it is a laboratory sample, not the sample of an air atmosphere, is analysed. The laboratory sample, in this case, is either a solid sorbent, a filter or a liquid absorber with an analyte sorbed from the air. Given this, it was decided that samples for proficiency testing should be created in a form similar to laboratory samples.

Importantly, samples must meet specific requirements. On the one hand, they should be homogeneous and stable during the whole period of laboratory proficiency testing. On the other hand, in addition to homogeneity and stability, good samples should be versatile, i.e. to be applicable in various measurement methods. Since laboratories participating in ILC studies exploit various techniques (included in their accreditation areas) for determining the same component in air environments, ILC providers undertake a great deal of work analysing all the methods applied. Testing techniques use different volumes of aspirated air, based on which the measurement range of the analyte content in a laboratory sample is calculated for every technique. Subsequently, the range that is common for all the methods measuring the analyte content is found. The analyte content in the sample under investigation must fall into this range. When creating a sample, account should be taken of the type of material used to absorb the analysed component (sorbents, filters, liquid absorbers); the methods applied for preparing samples for analysis (dry or wet ashing, etc.); the procedure used for calculating measurement results (measurement units); measurement methods (gravimetry, photometry, atomic absorption, etc.), as well as the amount of laboratory sample required for measurements.

The accumulated experience shows that the development of ILC samples for air quality testing is a time-consuming activity requiring not only the analysis of a large number of measurement methods, but also the corresponding qualification of specialists. On the basis of conducted studies (including the ILC research of air environments), UNIIM specialists develop stable, homogeneous and versatile ILC samples and RMs. At present, UNIIM is developing RMs for such indicators as iron, manganese, dust. The list of RMs will be expanded.

USE OF BISMUTH-CONTAINING GLASSY REFERENCE MATERIALS FOR THE DETERMINATION OF TRANSITION ELEMENTS BY THE LUMINESCENCE METHOD

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Keywords: bismuth-containing reference materials, transition elements, luminescent method of analysis

To analyze an enormous number of oxide materials, modern rapid analytical methods are used, the possibilities of which are limited by the absence of universal homogeneous comparison reference materials.

The most effective way of preparing such comparison reference materials is the glassy transition method. Bismuth-borate glassy reference materials were used previously as reference reference materials to determine the composition of complex oxide systems by the X-ray fluorescence method [1]. The introduction of rare-earth elements (REE) into the composition of glassy reference materials made it possible to determine by the luminescence method [2].

In this paper, we propose the use of bismuth-borate glassy reference materials for the determination of transition elements by the luminescence method. Luminescent analysis provides greater selectivity. The detection limits reached are usually $1\cdot10^{-6}$-$1\cdot10^{-4}$ % wt. for element-impurity in the analytical compounds.

The glassy reference materials were prepared using a bismuth-borate matrix by fusing it at T=1273-1373 K and post-calcination annealing at 673 K for 12 hours. REE and transition elements were introduced into the reference materials as oxides. Glassy reference materials consist of 70 % wt. Bi_2O_3, (30-X-Y) % wt. B_2O_3, X (0-2%) wt. Ln_2O_3 (Ln = Sm, Eu, Tb, Dy, Tm), Y (0-1%) wt. (Y=CuO, Fe_2O_3, Co_2O_3).

The microhardness of the reference materials was determined by the Vickers method. Its value was 450-490 N/mm^2.

The homogeneity of the glassy reference materials was determined by XSA, XSMA, spectrophotometric and luminescent methods, and also by the microhardness measurements. The homogeneity was determined by GOST 8.531 [3].

Resistance to environmental effects was estimated by R 50.2.031 [4]. The value of the certified characteristic of the reference material (RM) varied within the error of the RM under the conditions of storage and use for 3 years.

Luminescent researches of synthesized bismuth-borate glassy reference materials were carried out on the apparatus described in the monograph [5].

The luminescence spectrum of a glassy material that consists of 70 % wt. Bi_2O_3 and 30 % wt. B_2O_3 is a wide asymmetric band in the 400-600 nm region with a maximum corresponding to 520 nm by irradiation with light at wavelengths corresponding to the edge of the absorption band (T = 77 K). This spectrum is similar to the luminescence spectrum of bismuth-containing crystals with the ewlitin structure. The radiative process in bismuth-borate glassy materials can be attributed to the $^3P_0 \rightarrow {}^1S_0$ transition of Bi^{3+} and it is assumed that in the glassy materials there are the same clusters $[BiO_6]^{9-}$, as is the case in crystals with the ewlitin structure.

The luminescent properties of bismuth-borate glasses are successfully used for the phase analysis of bismuth-containing systems, and can be used in elemental analysis for the analytical

determination of luminescence quenching agents that suppress the emission of activators. Typical quenchers are Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, having in the absorption spectrum charge-transport bands whose maxima are in the ultraviolet region of the spectrum, but their intensity is so great that the tail of these bands extends into the visible and even (Fe^{3+}) into the near infrared region [6]. The charge transfer band extinguishes the glow of all activators whose emission bands are overlapped by it.

The quenching effect of the intensity of the exciton luminescence band of Bi^{3+} (λmax=520 nm) is established when individual oxides of transition elements (CuO, Fe_2O_3, Co_2O_3) are added to the bismuth-borate matrix. The Stern-Folmer equation adequately describes the quenching process and proves the participation of transition elements in recombination luminescence in bismuth-borate glasses and concentration quenching. The calibration dependences are plotted in the coordinates ln[(Io/I)-1]=f(lnC) (where Io and I are the luminescence intensity of Bi^{3+} in the material that does not contain and contains the ions of the transition element, respectively, and C is the ion concentration of the transition element in the material). The greatest effect of quenching of intrinsic luminescence of bismuth was observed for materials containing Cu^{2+} ions in the Cu-Co-Fe series approximately 1,5 times. Based on the established effect of quenching of the luminescence of bismuth ions by copper ions in bismuth-borate glasses, a method for low-temperature luminescence determination of copper content in high-temperature superconductors of various compositions Bi-Sr-Ca-Cu-O was developed and its metrological characteristics were evaluated. The error in the luminescence determination of copper in HTSC does not exceed 0,04 in relative units, the detection limit is 0,001 % wt.

Introduction of rare earth oxides (Sm, Eu, Tb, Dy, Tm) in the bismuth-borate matrix leads to a decrease in the intensity of the luminescence radiation of Bi^{3+} ions at 77 K, which also obeys the Stern-Folmer law. Equations of calibration dependences connecting the change in the luminescence intensity of Bi^{3+} ions from the REE content are obtained. The greatest change in the signal was observed in materials containing Sm^{3+} ions.

The possibility of using a luminescence method for determining elements in the composition of high-temperature superconducting oxide phases containing both REE ions and ions of transition elements was investigated. Glassy reference materials were prepared, into the matrix of which Dy_2O_3 (0,5 % wt.) and CuO (0,001- 0,25 % wt.) were introduced. The Dy_2O_3 content, equal to 0,5 % wt., corresponds to the maximum possible content in the range of the linear dependence of the intrinsic luminescence of Dy^{3+} on its concentration at room temperature. The luminescent properties of the obtained glassy reference materials were studied at temperatures of 77 and 298 K. It was found that a 90 % decrease in the luminescence intensity at 298 K is reached with Dy^{3+} content in the reference materials equal to 0,06 % wt. The calibration dependence in the logarithmic coordinates ln[(Io/I)-1]=f(lnC) is constructed to determine the copper content from 0,001 to 0,06 % wt. (where Io is the luminescence intensity of Dy^{3+} in a reference material that does not contain Cu^{2+} ions, I is the Dy^{3+} luminescence intensity in a reference material containing Cu^{2+} ions, and C is the concentration of Cu^{2+} ions). The influence of temperature on quenching by Cu^{2+} ions of fluorescent radiation Dy^{3+} is established. At T=298 K, quenching of the luminescence proceeds more intensively. An analysis of the spectra at 77 K showed that simultaneous quenching of the luminescent radiation of Bi^{3+} and Dy^{3+} by Cu^{2+} ions occurs. The method for luminescent determination of the copper content at room temperature was developed using bismuth-borate glassy reference materials doped with Dy_2O_3.

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HARMONISED GUIDANCE FOR THE PRODUCERS AND USERS OF REFERENCE MATERIALS – THE CURRENT STATUS AND FUTURE PROSPECTS

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Keywords: International Organization for Standardization, reference materials, Guide

ISO/REMCO, the ISO Committee on Reference Materials, has actively been updating its guidance documents over the past five years. Since the conversion of the third edition of ISO Guide 34 to the international standard ISO 17034 to address the conformity assessment of reference material producers, the work of the committee has focussed on the revision of ISO Guide 35 and the development of up to date guidance for the users of reference materials.

The prospects for the future work of the committee include the development of more field specific guidance. A few areas that have been identified include guidance for the preparation of qualitative reference materials. In 2015 a technical report (TR 79) was published containing a range of examples of qualitative reference materials and how they were prepared. At the beginning of 2018 a new work item proposal was approved for the development of a guidance document for the preparation of qualitative reference materials (ISO Guide 85).

A new work item proposal (ISO Guide 86) was also approved for the development of harmonised guidance for the preparation of high purity reference materials for small organic molecules. Furthermore, an ad-hoc working group has been established with the terms of reference to collect a repository of examples and information on the state of our knowledge related to high purity reference materials for inorganic elements.

In 2014, ISO Guide 80, a guidance document for the in-house preparation of quality control materials (QCMs) was published by the committee. QCMs are mostly used to monitor laboratory methods that have already been validated to be able to detect change or when a method goes out of statistical control. QCMs are RMs and as such must be sufficiently homogeneous and stable for the intended use.

The third edition of ISO Guide 33, "Reference materials – Good practice in using reference materials" was published early in 2015. The previous edition focussed on the use of certified reference materials. The new edition includes all types of reference materials and their uses. In the document the difference between certified reference materials and other reference materials is highlighted in terms of the different applications they can be utilised for based on their characteristics.

A brief introduction will be provided to the new editions of these and other guidance documents developed by ISO/REMCO.

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FORTHCOMING ENDEAVOURS OF ISO/REMCO

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Already for 41 years, REMCO is the Committee on reference materials of the International Standardization Organisation ISO. It develops and maintains guidance documents on the production and use of reference materials in general and certified reference materials in particular.

After a period of dense activities in converting a basic document, namely Guide 34, into an International Standard, and comprehensively revising all other basic documents (Guide 30 on Terms and Definitions, G31 on the Contents of Certificates, Guide 33 on Uses of RM, Guide 35 on Characterisation and Value Assignment to (C)RM, together with TR 79 on qualitative RM, and TR 16476 on metrological traceability), ISO/REMCO is in the phase of focusing on, and scrutinising, more specific issues in connection with reference materials. This includes pure inorganic and organic materials mainly designated to be used as calibration substances, and a completely new project considering specific requirements to reference materials used in process analytical technologies.

The talk will give an overview on the current endeavours of REMCO, making emphasis on the progress achieved within the numerous projects.

VALIDATION OF METHODS FOR THE DETERMINATION OF QUALITATIVE PROPERTIES

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Reference materials play a key role in external quality assurance of calibration and testing laboratories. Their production is governed by ISO/REMCO documents from Guide 30 to 35, and the International Standard ISO 17034 setting the requirements for the competence of reference material producers. One of the core requirements is a complete method validation for all methods used in RM production.

Approaches to method validation are well described, in a multitude of publications and text books, for quantitative analytical applications. Qualitative properties and their reliable determination are much less considered, although a minimum of half of all clinical analyses alone are purely qualitative. However, for qualitative assessments (as e.g. a pregnancy test or an assignment of IgB), clinical laboratories strictly follow the recommendations of the Chambers of Physicians in their countries, as e.g. in Germany the GI:FCP [1] In this connection, the paper will partially refer to the current edition of the GI:FCP.

Beyond this field of application, not much has been done (despite any efforts of ISO/REMCO) in the area of validation of qualitative methods.

The paper will describe some feasible approaches to validation of methods assigning a qualitative (nominal) property to an object (later on certified as a CRM), exemplified for a virus identification using a combination of four methods ELISA, RT-PCR, electron microscopy and Sanger sequencing.

ISO/REMCO is about the development of a more comprehensive guideline for these kinds of analyses.

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METROLOGICAL ASSURANCE FOR DIOXIN MEASUREMENTS. DEVELOPMENT OF A NEW CERTIFIED REFERENCE MATERIAL OF DIOXIN MASS FRACTION IN ANIMAL FAT

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Keywords: dioxins, calibration, validation, traceability, certified value, uncertainty, certified reference material, mass balance approach

Polychlorinated dibenzo-(p)-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are persistent organic pollutants (POPs) and are subject of Stockholm Convention. Among PCDD and PCDF the 17 congeners have got chlorine atoms in 2,3,7,8-positions in molecule (hereinafter - “dioxins”) and are characterized by a unique biological activity and can become one of the causes of long-term contamination of the biosphere. It is they are the subject of measurement.

Determination of “dioxins” in all types of matrices is not only a complex analytical task but also a particular problem in terms of metrological assurance of measurements.

Measurement of all organic compounds including “dioxins” by gas or liquid chromatography needs to use appropriate calibration standard and matrix reference materials with certified values of analytes for method validation and verification as well. Implementation for measurement and validation the metrological traceable standards an d materials guarantees not only high accuracy and reliability measurement results, but also the international recognition of measurement results (Convention CIPM MRA, 14.10.1999 [1]). Thus, the traceability to the reference units and/or to a National or International Standards is a key requirement for comparability of measurement results from different analytical laboratories.

As of today in Russia no traceable reference materials (hereinafter – RMs) of “dioxins” have been produced neither in the form of solutions, nor matrices. The lack of traceable RMs of “dioxins” is directly related to the feature of these organic compounds.

The base of traceability in organic analysis is pure organic substances with estimated mass fraction of the main component and appropriate uncertainty. The traditional and internationally recognized indirect method for determining the purity of organic compounds is the mass balance approach. This method is based on the measurement of four probable groups of impurities (related structure impurity, water, volatile organic compounds and non-volatile contents) and following calculation of the main component mass fraction by the equation “100 % minus sum of impurities”. Thus, the first necessary condition for the traceability chain creation is the pure organic substance in sufficient amount for its comprehensive study.

Pure organic substances of PCDD and PCDF, including 17 hazardous congeners, are not commercial products. Several foreign producers synthesize them in limited amount for analytical purposes only. In this situation “dioxins”, pure organic substances are hard-to-get and extremely expensive.

Today, the only available metrologically traceable means of measurement for dioxins (CRM status) is RMs produced by JRC-IRMM (Joint Research Centre - Institute for Reference Materials and Measurements). These CRMs are solutions of 17 native congeners and their $^{13}C_{12}$-labeled analogues in an organic solvent - nonane [2].

VNIIM has developed the matrix reference material with certified values of “dioxins” using the CRM JRC-IRMM solutions for analytical equipment calibration. Pork fat was chosen as adipose matrix, it could be entirely appropriate model for fat-containing foods.

The material for RM was prepared in Department of Measurement Standards and Investigations in the Field of Organic and Inorganic Analysis of VNIIM. Meat and bone meal contaminated with “dioxins” in a natural way was used for that. The fat fraction containing native “dioxins” was obtained from meat and bone meal by extraction and then was added into the molten pork fat. It liquid matrix was carefully homogenized and packaged in sealed glass containers.

The set of samples obtained in this way was investigated for homogeneity and stability in accordance with GOST ISO Guide 35—2015 [3]. The mass fractions of seven individual congeners of “dioxins” were certified.

The certified values are given in table 1.

T a b l e 1. Certified values of selected “dioxins”

Congeners	Mass fraction, ng/kg	The expanded uncertainty (k=2), ng/kg
2,3,7,8-TetraCDF	1,18	0,24
2,3,4,7,8-PentaCDF	823	76
1,2,3,4,7,8-HexaCDF	215	20
1,2,3,6,7,8-HexaCDF	116	13
2,3,4,6,7,8- HexaCDF	115	14
1,2,3,4,6,7,8-HeptaCDF	47,0	4,6
1,2,3,4,7,8,9- HeptaCDF	9,27	1,06

The experimental batch of RM was used for Interlaboratory Comparative Test, in which leading Russian and foreign laboratories participated.

The RM examination with the purpose of approval and the introduction this of RM in Federal Information Fund for equivalence of measurement is scheduled for 2019.

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THE USE OF A REFERENCE MATERIAL OF ASPHALT-CONCRETE MIXTURE IN THE EVALUATION OF PERSONNEL SKILLS AT A ROAD CONSTRUCTION LABORATORY

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Keywords: reference materials, control material, testing laboratory, quality control, skill, personnel involved in research (tests), control charts, risk calculation

According to the criterion for accreditation [1] of paragraph 20 and paragraph 23.11 in the laboratory, the rules for quality control of measurement results should be developed and implemented and the laboratory should have personnel participating in researches (tests) with a confirmed skill.

One of the methods for controlling the quality of measurement results is the use of control materials with which it is proposed to solve the task and assess the skills of the personnel of the testing laboratory. The use of control materials with reference values through their measurements will allow continuous monitoring of the personnel `s skill, since the control materials are uniform and stable in time.

The use of control materials is intended for laboratories engaged in physical and mechanical tests, because in their industry, they don’t have certified reference materials.

FSUE “UNIIM” has developed a procedure for assessing the skills of personnel using a control material.

We will consider the solution of this problem on the example of determining the average density of asphalt concrete mixture according to [2].

The source material for the development is a mixture of hot, fine grained, dense asphalt concrete (type B, grade 1). The assigned index is the average density chosen from among those given in [2].

This material was researched by the method of interlaboratory attestation according to [3], it was assigned a reference value of the mean density with an error $\rho m = (2.61 \pm 0.02)$ g/cm^3.

Measuring processes of the testing laboratory must be in a controlled state.

The task of statistical management of the measuring process is to ensure and maintain the process at a stable level. Control charts are the main statistical tool used.

The control map reflects the stability of the measuring process by the absence of points outside the control boundaries, trends and non-random behavior within the control boundaries.

To keep the process in a state of statistical manageability, we need to remove all possible causes that may affect the measurement result. The use of the same control material will allow carrying out measurements by the same procedure using the same metrologically provided measuring equipment under controlled external conditions.

In view of the above, the only reason for the instability of the measurement result is the operator's errors caused by the loss or deterioration of the personnel skills.

Consider the algorithm of the process in Figure 1.

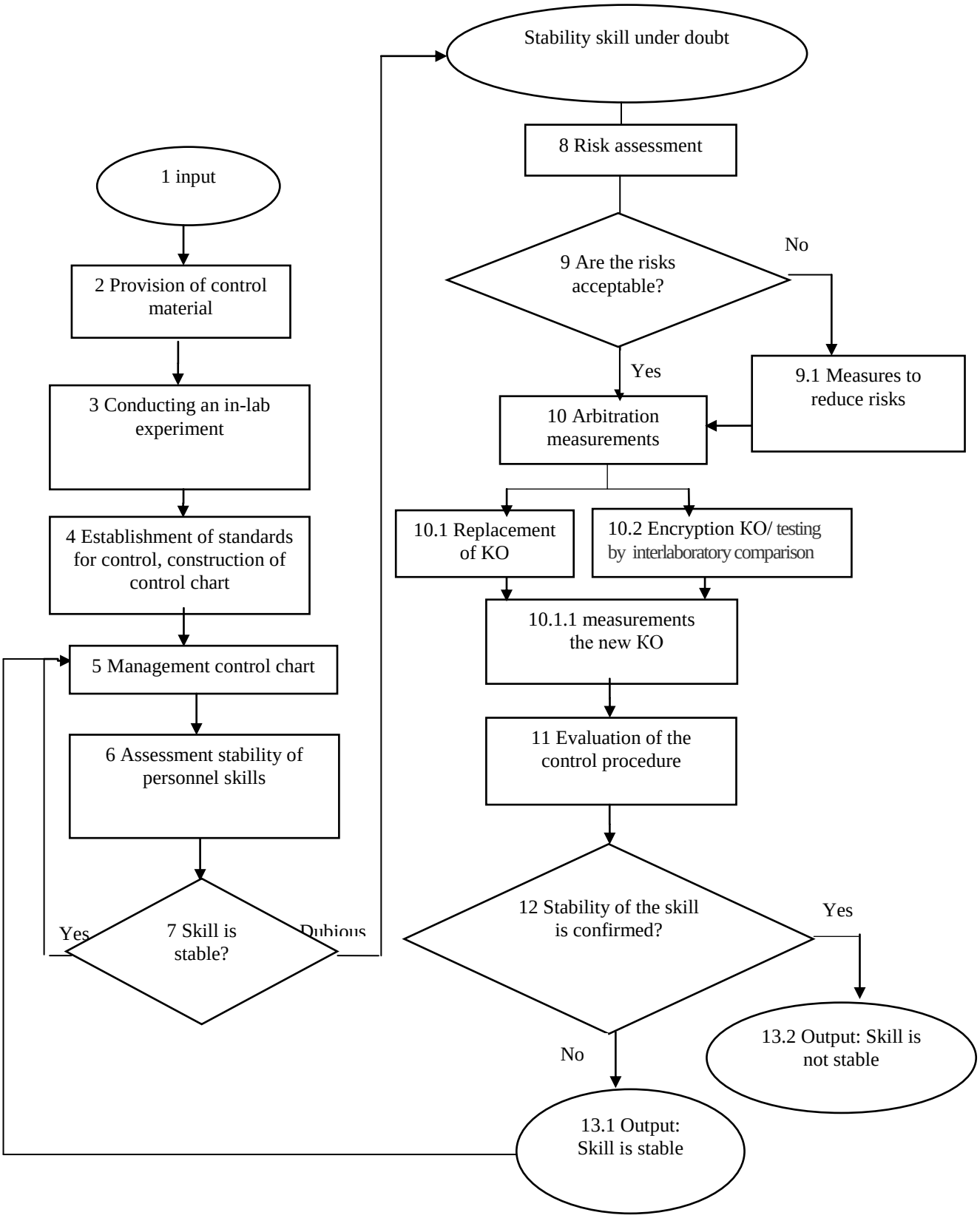

Fig. 1. Block diagram of the process of assessing the skills of laboratory personnel

1. Personnel (operator) should be subject to assessment of skills in order to meet accreditation

criteria.

2. The specialist responsible for evaluating the statistical characteristics of the measuring process (hereinafter referred to as the specialist) provides the operator with control materials from the certified batch of control materials of the asphalt concrete mixture.

If there are no conditions for doubtfulness of the skill (criteria of process variability), then the skill is recognized as stable and the control charts are maintained. If one of the criteria for non-stability of the process appears on the control chart, the skill of the operator is questioned and it becomes necessary to assess the risks that affect the process.

The specialist must identify the risks, that is, carry out the process of detection, recognition and description of risks. Identification includes the recognition of sources of risk, events, their causes and possible consequences.

Based on the result of risk assessment, a specialist draws up a risk register. He is also determines the criteria for the acceptability of risk. If risks are not recognized as acceptable, risk reduction measures should be taken. After undertaking risk reduction activities or if risks are initially recognized as acceptable, then arbitration measurements must be carried out.

There are two ways to assess the skill of the operator by the method of arbitration measurements.

1 The specialist replaces the control material of the asphalt concrete mixture on a control material with other assigned values.

2 The specialist encrypts the control material of the asphalt concrete mixture or organizes the participation of the laboratory in the ISI under the supervision of a third party (ISI provider).

The result of the arbitration measure is evaluated in a standard way. If the result is considered satisfactory then the stability of the skill is beyond doubt, otherwise the staff skill is recognized as not stable.

The developed process of personnel skills assessment in “UNII” testing laboratory is represented by a documented procedure and is an Appendix to the Instruction for the use of a control material.

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REFERENCE MATERIALS OF THE COMPOSITION AND PROPERTIES FOR DETERMINATION OF QUALITY PARAMETERS OF PETROLEUM AND PETROLEUM PRODUCTS

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Keywords: uniformity of measurements, VNIIM standard materials, reference materials, State primary measurement standard, viscosity, density

Uniformity of measurements of the composition and properties of substances and materials is ensured by the use of reference materials.

VNIIM standard materials (reference materials) is a generalized name for metrological products in the form of substances and materials developed and produced by D. I. Mendeleyev Institute for Metrology under the registered logo [1].

To ensure the quality of the reference materials produced by VNIIM, the institute has implemented a management system that meets the requirements of GOST ISO / IEC 17025-2009 “General requirements for the competence of testing and calibration laboratories” and ISO Guide 34:2009 “General requirements for the competence of reference material producers”.

Laboratory of viscosity and density at D. I. Mendeleyev Institute for Metrology is the custodian of the State primary standard of the unit kinematic viscosity liquid (GET 17-96) and the State primary standard of the unit density (GET 18-2014).

The history of the establishment of the laboratory dates back to the founding of the Main Chamber of Weights and Measures in the city of St. Petersburg. The first head of this institution also carried out fundamental studies of the density of water, air, mercury, and his followers were D.I. Mendeleyev, B.M. Kollovich, M.D. Ippits. The first publications relating to the activities of the laboratory date back to 1924.

Questions of measuring the viscosity in D. I. Mendeleyev Institute for Metrology began to be intensively engaged since 1938. Over the past years, studies have been performed that make it possible to establish the unity of viscosity measurements in the Russian Federation. This uniformity is ensured by the development and introduction into practice of standard, exemplary and working viscometers.

Since the late 90's, along with the creation and improvement of standards, the laboratory conducts research projects aimed at developing reference materials of parameters for the quality of oil and petroleum products. To date, the laboratory produces 12 categories (105 types of materials), presented in Table 1, which are used in the system for ensuring the uniformity of measurements for:

– transfer of measurement units from state primary standards to working standards in accordance with verification schemes;

– for graduation and calibration of measuring instruments;

– for control of metrological characteristics of measuring instruments during their verification and testing, including during tests for the purpose of type approval;

– for the estimation and control of the accuracy of measurements performed by measurement procedures, when developing, evaluating and applying;

– for the certification of testing equipment;

– to control the quality of measurements (tests, analyzes) in the accreditation of laboratories and in the inspection of their activities [1, 2].

Reference materials (Figure 1), produced by the laboratory, are based on the VNIIM reference base, they carry reliable information on the physicochemical properties and composition of various controlled substances such as viscosity, density, absolute saturated vapor pressure, mass fraction of water in oil and oil products, etc.

Fig. 1. General view of reference materials produced by D. I. Mendeleyev Institute for Metrology

T a b l e 1. List of categories of reference materials produced by Laboratory of viscosity and density

Name	Denotation	Number of types
Viscosity reference materials	GSO REV	21
Density reference materials	GSO REP	15
Absolute pressure of saturated vapor of petroleum products reference materials	GSO ADNP	6
Content of chloride salts in petroleum and petroleum products reference materials	GSO HSN-VNIIM	6
Mass fraction of sulfur in in petroleum and petroleum products reference materials	GSO SN-VNIIM	15
Content of trace sulfur in petroleum products reference materials	GSO SSN-VNIIM	6
Mass share of mercaptan sulfur in petroleum products reference materials	GSO MSN-VNIIM	10
Flash point of petroleum products in a closed crucible reference materials	GSO TVZT-VNIIM	5
Flash point of petroleum products in open crucible reference materials	GSO TVOT-VNIIM	2
Mass fraction of mechanical impurities in in petroleum and petroleum products reference materials	GSO MPN-VNIIM	8
Mass fraction of water in in petroleum and petroleum products reference materials	GSO VN-VNIIM	10
Mass fraction of water in organic liquid reference materials	GSO VF-VNIIM	1

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ACTIVITY OF VNIIFTRI IN THE FIELD OF PHYSICAL-CHEMICAL MEASUREMENTS

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Keywords: measurement standard, comparison, pH, pX, standard-titer, buffer solution, reference material, type approval, calibration, verification, certification of measuring procedure, certification of cleanroom, production of reference materials and measures

According to the VNIIFTRI accredited scope in the field of physicochemical measurements, NIO-6 (the Research Department of Physicochemical and Electrical Measurements, VNIIFTRI) carry out measuring instruments (MI) type approval and Reference materials, verification / calibration of MI, certification of measurement procedures, certification of cleanrooms, etc. Actively takes part in the work of Technical Committees, Subcommittees and Working Groups of Rosstandart, interstates, regional and international organizations.

In addition, scientific research in assigned scope of VNIIFTRI is being carried out at NIO-6 ensuring on the transfer of units from state primary standards to other measurement standards and measuring instruments.

As known, measuring instruments of pH by their number and type occupy one of the first places among liquid analyzers. There are several million devices in the Russian Federation. Today, the determination of the pH is the most demanded method for controlling the composition of aqueous solutions and other liquid media. The pH is the most important physicochemical characteristic that determines the basic acid-alkaline properties of solutions. These measurements are used in almost all spheres of human activity.

It should be noted that VNIIFTRI is the leading Russian institute in the fields of pH and pX measurements in aqueous solutions. At the head of the State Hierarchy of the pH measuring instruments is GET 54-2011 [1].

At present, on the basis of NIO-6, the production of standard titres of the 1st and 2nd order, which use for the preparation of buffer solutions. As well as buffer solutions of the 2nd order, is established for the purpose of reproducing and transfer pH units (1-12) from the state primary standard to the secondary standards and measuring instruments in this area. All products were tested for type approval, included in the State Register of Measuring Instruments and approved for use on the territory of the Russian Federation.

At the head of the State Hierarchy of the Measuring instruments used electrochemical methods to determine the ionic compounds of aqueous solutions (measuring instruments of RX) is GET 171-2011 [2].

It should be noted that VNIIFTRI is a unique organization in Russia, that produces mono-element solutions - working measurement standards for the activity of Na^+, K^+, F^-, Cl^-, Br^-, I^-, NO_3^- (pX) ions in aqueous media.

However, the institute did not stop there and continues expanding the list of units of pH and pX by scientific research, key and pilot comparisons with the world's leading metrology institutes specializing in this field of measurement.

As a result of successful participation of a Russian new state primary standard of mass fraction and mass (molar) concentration of inorganic components in aqueous solutions

“GET 217-2018” in international supplementary comparisons within the framework of BIPM (IAWG CCQM BIPM), NIO-6 is carrying out the development of production methods of reference materials of heavy metals in aqueous solutions for transferring the units from the primary standard to high-precision instruments in physicochemical area [3].

Also, the advanced state primary standard of disperse parameters of aerosols, suspensions and powders “GET-163” is taking part in international pilot comparisons in the field of nanoparticle measurements within the framework of the BIPM. With the positive participation of GET-163 in the comparisons in NIO-6, work will begin on developing methods for obtaining materials of micro- and nano-particles in various matrices.

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VNIIFTRI'S PARTICIPATION IN INTERNATIONAL COMPARISONS IN THE FIELD OF PHYSICAL-CHEMICAL MEASUREMENTS

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Keywords: international comparison, state primary standard, physicochemical measurement, pH, pX, mass spectrometry, measuring and calibration capability, standard-titer, buffer solution, reference material

The Research Department of Physical-chemical and Electrical Measurements of FSUE “VNIIFTRI” (NIO-6) is the holder of 6 State primary standards and actively participates in international and regional comparisons in order to maintain the reference base and ensure the uniformity of measurements in Russia in the field of physical-chemical measurements at the level of modern international requirements

Today, here are three of the six State primary standards of NIO-6:

The State primary standard of pH in aqueous solutions (GET 54-2011);

The State primary standard of pX in aqueous solutions (GET 171-2011);

The State primary standard of inorganic components mass fraction and mass (molar) concentration in aqueous solutions, using gravimetric and spectral methods (GET 217-2018), that demonstrated their calibration and measuring capabilities in CCQM in international key, additional and pilot comparisons at the level of the leading and world-renowned metrology institutes:

- ✓ CCQM-K48.2014. Key comparison. Assay of Potassium Chloride [1];
- ✓ CCQM – P152.2014. Pilot Study. Acidity function of phthalate buffer in water/ethanol mixture (mass fraction 50%), Draft A;
- ✓ CCQM – K99. 2015. Key comparison on pH of an unknown phosphate buffer [2];
- ✓ APMP.QM-K91. 2016 APMP comparison on pH measurement of phthalate buffer [3] ;
- ✓ CCQM – K18. 2016. Key comparison pH of carbonate buffer, Planned;
- ✓ CCQM-K19.20XX Key Comparison on Borate Buffer, Planned;
- ✓ SIM.QM-S7 Supplementary Comparison. Trace Metals in Drinking Water [4] ;
- ✓ APMP.QM-S10 Supplementary Comparison. Elements in Food Supplement. Measurement completed;
- ✓ EURAMET.QM-S11 Supplementary Comparison. Elements in River Water. Protocol completed;
- ✓ CCQM-K128. Key comparison. Measurement of Heavy Metals and Organo-Tin in Leather Powder. In progress;
- ✓ CCQM-K145 Key comparison. Toxic and essential elements in bovin liver powder. Planed;
- ✓ CCQM-K155 and P196: Elements in seawater. Planned.

The state primary standard of units of disperse parameters of aerosols, suspensions and powder materials of GET 163, improved in 2015-2017, actively joined international comparisons and plans to participate in two projects in 2017.

Moreover, it intends to participate in two joint comparison projects of GAWG and IAWG CCQM BIPM.

The State primary standard of the ionized air electric charge volumetric density and the aeroions number concentration (GET 177-2010) and the State primary standard of oxygen and

hydrogen mass concentration in liquid media (GET 212-2014) acted as coordinators in COOMET regional pilot comparisons.

Today, the production of primary and secondary standard titers and buffer solutions of pH, standard-titers of ORP, acidity measures, and working standards for ion activity in aqueous solutions is established at the NIO-6. Due to the fact, that the standards confirmed their measurement capabilities at the international level (5 SMS-lines in the BIPM KCDB database on the calibration and measurement capabilities of national (state) institutes), FSUE VNIIFTRI may declare with confidence about high quality of its products.

As a result of the positive participation of the GET 217-2018 in the international additional comparison of SIM.QM-S7 “Residual amounts of metals in drinking water”, in 2018, VNIIFTRI received four new lines for determining the mass fraction of residual amounts of metals in drinking water with the corresponding uncertainties measurements, with a confidence level of 95 % and a coverage ratio of k=2:

- ✓ Cu (Cupper) 1-100 µg/kg, expanded uncertainty 0,11-8 µg/kg;
- ✓ St (Strontium) 1-100 µg/kg, expanded uncertainty 0,05-3,5 µg/kg;
- ✓ Pb (Lead) 0,1-100 µg/kg, expanded uncertainty 0,015-10 µg/kg;
- ✓ Na (Sodium) 0,5-50 mg/kg, expanded uncertainty 0,035-2,5 mg/kg;

The received recognition of the measurement capabilities of GET 217-2018 in the specified ranges with the specified uncertainties will allow NIO-6 to establish production of relatively inexpensive domestic reference materials of copper, strontium, lead and sodium metals in aqueous solutions traceable to CMC lines and having characteristics not inferior to foreign analogs.

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ABSORBED DOSE RATE AND ABSORBED DOSE TRANSFER REFERENCE MATERIALS WITH DOSE MEASUREMENT POSSIBILITIES RANGING FROM 50 TO 1000 Gy

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Keywords: Ionizing radiation, radiation processing technology, radiation processing plant, absorbed dose (AD) rate (ADR), product safety, medical device sterilization, food processing, radiation resistance, radiochromic film, absorbed dose certified reference material (AD CRM), technical agreement, fading, heat treatment

In radiation processing technology (RPT) the purpose of the irradiation process (e.g. medical device sterilization [1-4], food processing [5-8], radiation resistance of electronic devices, polymer crosslinking by ionizing radiation, nanotechnology etc 9.) achievable only by establishing the process parameters under practical processing conditions. The irradiation energy characteristics, packaging of processing product, its orientation within the package and with respect to the irradiator location as well, speed of conveyor and its path shall be specified. The absorbed dose (AD) measurement procedure determines suitable process definition, which is the keystone for the proper radiation processing. The dose range approach should be made in accordance with applicable regulatory requirements, radiation-processing instructions for each type of product to be processed. Dosimetry monitoring during irradiation and carry out the dose mapping insight product, dose distribution before and after source replenishment work responsible for quality control of incoming and outgoing product to comply customer specifications.

In the Russian Federation for dosimetry purposes in radiation technologies the certified reference materials (CRMs) on the base of radiation sensitive films issued by VNIIFTRI are in the inventory. These CRMs have absorbed dose measurement possibilities with a well-defined traceability linkage to existing VNIIFTRI dedicated primary absorbed dose rate unit primary standard for radiation technologies (GET 209-2014). This traceability linkage is established via criteria and protocols defined by VNIIFTRI for AD at (1-200) kGy to meet the needs of the dosimetry at high level of AD e.g. sterilization of medical devices and polymer crosslinking.

Nowadays for control of agricultural products and food processing in all types of ionizing radiation facilities involves the use of accepted measuring methods of the absorbed radiation dose, that dose distribution in the product package, and monitoring of the physical parameters of the process.

For adequacy of food irradiation technology careful dosimetry is required to ensure that a technologically useful dose interpretation range (0,05 kGy – 50 kGy) has been applied for maintaining the best possible dose uniformity ratio. For particular technical purpose to be released the irradiation uniformity ratio shouldn't exceed the value Dmax/Dmin =3 and the mapping dose range for any product item should be satisfied condition

$$D_{min} \leq D_{irrad} \leq D_{max},$$

where

- Dmin - lower bound absorbed dose value for technical purpose achievement by irradiation;
- Dirrad - absorbed dose released insight product in accordance with dose mapping;
- Dmax - highest possible absorbed dose nondestructive for product quality.

A VNIIFTRI dosimetry experience in ionizing radiation processing plants with electron accelerators, radionuclides or bremsstrahlung shows that best measuring devices for routine dose monitoring in radiation technologies are radiation sensitive film based CRMs. The radiochromic film reference materials (RFRM) have high practical use owing to dose measurement simplicity by them, availability, reasonable price, and most promising dosimeters for widest available AD range to be certified. The RFRM can be used for both transfer and routine dosimetry with less expensive and user-friendly read-out optical density measuring equipment than on an alanine based EPR spectrometric dosimetry. The radiation sensitive films are irreplaceable for high-resolution absorbed dose distributions measurement of electron beam profiles and spatial depth doses, as well as dose distributions in thin layers and on surfaces of irradiated materials.

New developments in radiation sensitive films. Firstly we have shown that VNIIFTRI approved reference materials namely “CRM – 1 to 10 kGy”, “CRM – 5 to 50 kGy”, “CRM – 30 to 200 kGy” could be used as transfer and routine dosimetry systems in dose ranges of response from down of 50 up to 106 Gy. They are reading spectrophotometrically at certain wavelengths corresponding to multiple broad radiation induced absorption bands, which allows dose readings over a relatively broad dose range. These systems exhibits insignificant (accountable) dependence of response on temperature during as irradiation as readout, small dependence on relative humidity and ambient ultraviolet light (≤ 1 % to uncertainty) including small fading. Major advantages of radiation sensitive films are broad range of response (from 10th to 106 Gy), their wide availability in large relatively inexpensive batches and their ability to map both gamma ray and electron dose distribution with high spatial resolution (with less than 1 mm resolution).

Another investigated useful new radiation sensitive material is a complex on the base of coloring agents as Rhodamine C or azo dyes, which shows changes in its optical density upon ionizing radiation absorbed dose from 10-th of Gy and more.

New version of reference materials would be developed to extend the dose ranges of CRM for absorbed dose rate transfer in the range of 50 Gy to 103 Gy with an absorbed dose measurement possibility.

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DEVELOPMENT OF REFERENCE MATERIALS IN THE FIELD OF PHYSICAL AND CHEMICAL ANALYSIS. REFERENCE MATERIALS FOR COMPOSITION OF ALUMINUM, INDIA, MAGNESIUM, NICKEL AND TITAN AQUEOUS ION SOLUTIONS

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Keywords: reference material, spectral methods, GET 196-2015, state primary standard, aluminum, nickel, magnesium, titanium, indium, chemical analysis

Reference material – the material rather homogeneous and stable concerning certain properties to use it at measurement or at estimation of qualitative and quantitative properties of various materials according to alleged appointment. [2] Reference materials are the most important instrument for ensuring of the qualitative and quantitative chemical analysis. They are used for calibration, checking and tests of measuring instruments, including for type approval, certification and development of measurement procedures and reference measurement procedures, assessment of statistical characteristics of measuring process, intralaboratory quality control, external assessment of quality, etc.

VNIIOFI is a developer and the keeper of the State primary standard of units of a mass (molar) fraction and mass (molar) concentration of components in liquid and solid substances and materials on the basis of spectral methods (GET 196-2015). Tests for development of reference measurement procedures [1] and certification of reference materials are made on a standard of GET 196-2015 for such priority fields of the Russian industry as aircraft industry, mechanical engineering, ferrous and non-ferrous metallurgy, etc. [3].

Due to the raising requirements to quality of the industry of production made by the enterprises of these areas, the standard also has to provide the increased accuracy of reproduction and transfer of units of a mass (molar) fraction and mass (molar) concentration of components in liquid and solid substances and materials. As the methods realized in GET 196-2015 are indirect, they demand application of the certified reference materials for calibration the installations which are a part of a standard. One of the strongly influencing factors on the expanded measurement uncertainty is uncertainty of the certified value of units of reference materials. For the tasks set for VNIIOFI, the accuracy of certified reference materials offered in the Russian market is unsatisfactory.

For the solution of a current problem on the reduction of a contribution of certified reference materials’s uncertainty of certified reference materials in expanded uncertainty of measurements of a standard GET 196-2015 of VNIIOFI have been developed certified reference materials of composition of ions of metals (aluminum, magnesium, nickel, titanium, indium) with the required characteristics. These metals have been chosen as the most widespread elements which are present at matrixes of the main aviation alloys. Indium is also widely applied in the spectral analysis as the internal standard.

Metrological characteristics of the developed certified reference materials of composition of water solutions of metals are provided in Table 1.

T a b l e 1. Metrological characteristics of certified reference materials of ions of metals

CRM name	Metrological characteristics	
	mass concentration of ions, g/dm^3	expanded uncertainty of certified value with coverage factor k=2, %
Reference material of nickel ions	0,95-1,06	not more than 0,8
Reference material of aluminum ions	0,95-1,06	not more than 0,8
Reference material of indium ions	0,95-1,06	not more than 0,8
Reference material of magnesium ions	0,95-1,06	not more than 0,8
Reference material of titanium ions	0,95-1,06	not more than 0,8

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METHODOLOGICAL APPROACHES TO STATISTICAL EVALUATION OF TEST RESULTS OBTAINED DURING CERTIFICATION OF REFERENCE MATERIALS USED FOR BIOLOGICALS QUALITY EVALUATION

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Keywords: branch reference material, reference materials used for biologicals quality evaluation, biological reference materials, statistical methods

The lack of regulatory and procedural guidelines on certification of reference materials used for biologicals quality evaluation (hereinafter – BRMs) in Russia calls for the development of general principles of BRM certification, including methodological approaches to calculation of metrological characteristics on the basis of international guidelines [1], recommendations of the State System for Ensuring Uniform Measurement (SSM) [2], and taking into account specificity of biological medicinal products [3,4], and requirements of the State Pharmacopoeia of the Russian Federation and foreign Pharmacopoeias [5,6,7].

Since biological reference materials can be of various nature, there is no single algorithm for determination and calculation of a BRM certified parameter. A certification procedure has to be developed for every individual reference material taking into account specificity of the BRM material and methods used for determining the certified parameters. The authors propose a general certification strategy in one of their papers [8].

We propose the following algorithm for statistical analysis of test results obtained during BRM certification:

- determine the type of distribution of test results;
- assess the possibility of pooling the data;
- check for outliers;
- calculate the certified parameter of the reference standard;
- calculate the uncertainty of the certified parameter of the reference standard.

Determination of the type of distribution of test results:

Use statistical software (Microsoft Excel, STATISTICA 6.0, etc.) to assess the conformity of the obtained results to normal distribution according to Kolmogorov-Smirnov criterion (for the sample size $n > 50$) or Shapiro-Wilk criterion (for the sample size $n < 50$).

If the statistical test value is lower than the tabulated value for a corresponding number of degrees of freedom (df) which is the number of test results minus 1($df = n-1$), then the distribution of test results is close enough to normal distribution and Type A evaluation of standard and expanded uncertainties may be used [2,8].

If any set of data obtained during the RM certification does not fit a normal distribution, one has to use non-parametric statistical tests, e.g. Mann-Whitney test, to assess the uniformity of test results obtained by different operators [9].

Assessment of the possibility of pooling data.

Use Student’s t-test and F-test to assess the statistical significance of differences in the RM certified parameter values obtained by different operators [9]. Consider the following example of

statistical evaluation of test results obtained by two operators during BRM certification under intermediate precision conditions, where $n_1 = n_2 = 10$ results.

The criteria of statistical equivalence of the results obtained by the operators are:

$$t_{op1,2} \leq t\ (P;\ n_1 + n_2 - 1); \quad , (1)$$

$$F_{op1,2} \leq F\ (P;\ n_1 - 1; n_2 - 1), \text{where} \quad , (2)$$

$t_{op1,2}$ – t-test values calculated for the RM certified parameter measurements obtained by each operator;

$F_{op1,2}$ – F-test values calculated for the RM certified parameter measurements obtained by each operator;

$t\ (P;\ n_1 + n_2 - 1)$; $F\ (P;\ n_1 - 1; n_2 - 1)$ – tabulated values of Student’s t-test and F-test for the chosen confidence level P and the corresponding number of degrees of freedom.

Check for outliers.

When performing RM certification one may obtain outlying results. They may arise due to improper performance of the procedure or inadequacy (specificity) of the procedure itself.

If an outlier is shown to have arisen due to operator error, equipment error, calculation error – in other words, due to improper performance, it should be excluded from calculations.

If an outlier is attributable to the inadequacy of the procedure, the system suitability criteria (acceptance criteria for results) need to be revised, and if an outlier is attributable to the specificity of the procedure, an adequate number of replicates and the principle for excluding results from consideration have to be established.

The State Pharmacopoeia of the Russian Federation and foreign pharmacopoeias offer different approaches to checking obtained results for outliers [6,10,11]. Some examples are given below. In all of the cases the data are assumed to have normal distribution.

1. Three-sigma rule. Calculate the arithmetic mean ($\bar{X} = \frac{1}{n}\sum_{i=1}^{n} X_i$) and the sample standard deviation ($s = \sqrt{\sum_{i=1}^{n_1} \frac{(X_i - \bar{X})^2}{n-1}}$) for the BRM certified parameter as described in OFS.1.1.0013.15. Then calculate deviations (δ_i) of each X_i value of the certified parameter from the mean $\bar{X}$:

$$\delta_i = X_i - \bar{X} \quad , (3)$$

Leave out X_i values for which $|\delta_i| > 3 \cdot s$ [6].

2. Grubbs’ test. Normalize each X_i value by subtracting the mean $\bar{X}$ value from each X_i value and dividing this difference by the standard deviation s: $X_{norm} = \frac{(X_i - \bar{X})}{s}$. Choose the maximum absolute value X_{norm} and compare it to the tabulated critical value λ [11], chosen based on the sample size n and acceptable significance level (e.g., 5%). If the maximum X_{norm} value is greater than the tabulated λ value, then the corresponding X_i value is considered a wild observation and excluded from calculations of the BRM certified parameter [11]. Repeat the procedure for other outlying results.

3. Dixon’s test. Arrange the results by magnitude (i.e. X_n – is the maximum value, X_{n-1} – is the next value in terms of magnitude, etc., and X_1 – is the minimum value in terms of magnitude). For X_1 to be considered an outlier, calculate the ratio rcalc using the following formula, e.g. for a sample size n = 8…10:

- when an outlier is a minimum value:

$$r_{calc} = \frac{X_2 - X_1}{X_{n-1} - X_1}; \quad (3)$$

- when an outlier is a maximum value:

$$r_{calc} = \frac{X_n - X_{n-1}}{X_n - X_2}. \quad (4)$$

Compare the obtained rcalc to the tabulated critical value rtable [11] for a particular sample size (e.g., n=10) and the chosen significance level (e.g., 5 %). If the rcalc value is greater than the rtable, 0,05 value, it is considered as an outlier and excluded from calculations [10].

Dixon’s test is used for a sample size ranging from 3 to 13, but for the sample sizes n=3…7 and n=11…13 the formulas for rcalc calculation will differ from those given above. For a sample size of n > 13 Grubbs’ test is preferred [11].

Calculation of the BRM certified parameter.

After checking the data set for outliers and analyzing the possibility of pooling data obtained by different operators, calculate the BRM certified parameter (A), as the arithmetic mean of the whole data set.

If the biological activity of the reference material is expressed as titer, e.g. determined in the hemagglutination-inhibition reaction, the BRM certified parameter is taken as the median (Med) of a data set arranged in ascending order.

Calculation of uncertainty of the BRM certified parameter.

Certification of BRMs involves the use of biological, immunological, microbiological and other empirical methods [12, 13], in which case it is impossible to draw a demarcation line between the systematic and accidental components of the standard uncertainty as it is required for a step-by-step approach [14]. Experience gained during BRM certification [13] showed that when estimating uncertainty of BRM certified parameters it is better to use a “global approach” and assess the standard uncertainty based on the standard deviation (s) of results obtained under intermediate precision conditions [13]. The outcomes of using BRMs in biologicals quality control support the viability of this approach [16, 17].

Type A evaluation of expanded uncertainty of BRM at the confidence level 0.95 normally assumes a coverage factor k = 2.

In some cases the results of determination of the BRM certified parameter do not fit a normal distribution. This usually holds true of samples that were certified using such methods as hemagglutination-inhibition reaction [18,19].

If the value of the BRM certified parameter is expressed as median Med, the range of values may be determined according to GOST R ISO 16269-7 - 2004 requirements:

$$A_{min} = X_k \quad , (5)$$

$$A_{max} = X_{n_1+n_2-k+1} \quad , 6)$$

, where:

- k - order statistic value used for determination of confidence limits of the BRM certified parameter median.

A_{min} - lower confidence limit of the BRM certified parameter median at 95 % confidence;

A_{max} - upper confidence limit of the BRM certified parameter median at 95 % confidence.

For instance, in the case of 95 % confidence level and sample size $n_1 + n_2 = 20$, k = 6 [20]. Subsequently, $A_{min} = X_6$, $A_{max} = X_{15}$, i.e. the BRM certified parameter is somewhere between the 6th and the 15th elements of the experimental data array.

Thus, due to complexity and variability of biologicals composition, and differences in the underlying mechanisms of test methods, an individual approach is required for calculation of BRM metrological parameters (i.e. of the certified parameter value and associated uncertainty).

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PROCEDURES FOR THE MANAGEMENT OF REAGENTS AND REFERENCE MATERIALS AT THE LABORATORY IN ACCORDANCE WITH ISO / IEC 17025:2017

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Keywords: laboratory accreditation, general requirements for laboratory competence, laboratory resource management, use of reference materials and reagents, traceability, metrology, risk assessment, reliable test results

A new version of ISO/IEC 17025:2017 [1] was adopted in November 2017. A transitional period of 3 years has been declared. This means that the inspection control of accredited laboratories from the end of 2020 will be held according to the new version of the standard, and the primary accreditation from the beginning of 2019. These rules are established by different accreditation bodies individually. One of the changes in the new version of the standard affects the management of standards, reference materials and reagents. Now the requirements for them are described in the chapter on resource management (6. Resource requirements), section: equipment (6.4 Equipment). Some of the requirements in the previous version were only for equipment, and in the current version they apply to all resources. In particular, the new version of the standard sets the following requirements for standards, reference materials and reagents. There should be rules for managing measurement standards, reference materials and reagents that are outside the permanent control of the laboratory, for example, transfer to a lease or lease. The requirements for the presence of labels or other types of identification, for the control of period of validity, have been submitted. There should be a system for monitoring proper storage conditions, as well as a system for managing resources of unknown quality as a result of improper storage or use, as well as procedures for assessing the impact of this resource on work already done. Requirements are formulated for the availability of records for working with measurement standards, reference materials and reagents in particular: identification (name of the manufacturer, lot, serial number, etc.); data on the incoming control; current location, where appropriate; approval dates, certified values and designation of reference materials, acceptance criteria and expiration dates. And one of the most important requirements of the laboratory is to ensure the traceability of measurement results using certified values of certified reference materials with the specified metrological traceability to SI units or the certified value of a certified reference materials obtained from a competent producer. The standard clarifies that producers of reference materials that meet the requirements of ISO 17034:2016 (en) “General requirements for the competence of reference material producers” are considered competent.

Thus, to implement a new version of the standard and successfully pass the inspection control or accreditation, it is necessary to revise its own management system, procedures for managing reference materials and reagents, to revise the nomenclature of current resources and, if necessary, to purchase resources corresponding to the new standard. Realization of these requirements allows to demonstrate the traceability of results in the laboratory and to obtain reliable results of measurements and tests.

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PROBLEMS OF DOSIMETRY AND NEUTRON RADIATION SPECTROMETRY

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Keywords: neutron radiation, neutron radiation dosimetry, spectrometry of neutron radiation, a multi-beam spectrometer, detectors of neutron radiation, medicine, metrological provision, boron neutron capture therapy, energy dependence of sensitivity

The solution of these problems is today a priority task of metrology. The use of neutron radiation in the absence of a reference database and regulatory documents can lead to an incorrect determination of the physical quantity, which can harm a person. Separately affecting the medical industry: in boron-neutron capture therapy the object of exposure is a person. Therefore, this technology must be taken seriously and take into account all sorts of factors.

To provide radiation monitoring for personnel of nuclear power plants, the task of determining the neutron spectrum also remains open. The presence of premises with an increased radiation level at the nuclear power plant creates the problem of determining the dose characteristics for station staff.

With the problem of reconstructing the spectrum of neutron radiation, they collide in research reactors and some installations, where the application of the activation-foil method becomes unacceptable. At a flux density of $\approx 10^8$-10^{10} neutron $\cdot$ s^{-1} or less, a number of limitations arise that lead to an increase in the error.

In connection with the increase in demand and the expansion of the areas of application of neutron radiation, the development of the nuclear industry and medicine, it is necessary to develop and introduce methods for the spectrometry of neutron radiation that permit the calibration of measuring instruments in fields closest to real fields.

As part of the research VNIIFTRI developed a model of neutron spectrometer on the basis of Bonner spheres. Various scintillation detectors and gas-filled counters were used as the neutron detectors, which is described in more detail in [1]. By sharing scintillators and gas-meter the spectrometer active unit is able to reproduce ambient equivalent dose with high precision under conditions close to real.

Thus, it becomes possible to assess the detrimental effects of neutron radiation on the human body when conducting boron neutron capture therapy. The use of the developed spectrometer will help evaluate the component of the harmful effect of the high-energy component of the neutron spectrum, help improve facilities and create more efficient beam formers for more successful application and development of this direction in the country.

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ORGANIZATION OF INTERLABORATORY COMPARISONS FOR DETERMINING THE INDICATORS OF THE COMPOSITION AND PROPERTIES OF DRINKING, NATURAL AND PURIFIED WASTE WATER USING REFERENCE MATERIALS

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Keywords: interlaboratory comparisons, proficiency testing, ICT provider, reference material, metrological traceability

The list of indicators, characterizing the natural water’s pollution degree, for which in Russia the values of maximum permissible concentrations are established, contain a significant number of inorganic substances. Analysis of samples of natural, drinking and waste water for the content of inorganic anions, technogenic metals and such properties as chemical and bacteriological oxygen consumption is one of the most common types of industrial and state environmental control. The results of measurements obtained by chemical ecological laboratories are used for conclusions about the quality of drinking water, the state of natural water bodies, and the composition of discharged sewage.

In accordance with GOST ISO/IEC 17025-2009 [1] accredited laboratories must confirm the ability to perform the relevant measurements with the required accuracy. The most obvious evidence of this ability is the documented positive results of the laboratory's participation in interlaboratory comparisons conducted with purpose of proficiency testing.

In accordance with GOST ISO/IEC 17043-2013 [2], interlaboratory comparisons are the organization, performance and evaluation of measurements or tests of the same or similar samples by two or more laboratories in accordance with pre-established conditions. When conducting the quantitative program of interlaboratory comparisons the participant’s of measurement result accuracy is compared with demands established in the measurement procedures or directly in the program.

Ural Research and Scientific Institute for Metrology (UNIIM) is an accredited provider of interlaboratory comparisons (Accreditation Certificate RA.RU.430158 dated July 20, 2016). The scope UNIIM’s activity includes many environmental objects and natural, drinking and waste waters among them.

The reliability of the provider's conclusions about the quality of the participants' measurement results mostly depends on the samples used. The provider must ensure the homogeneity and stability of the sample material and the accuracy of establishing the values of the monitored indicators. This is especially important when conducting interlaboratory comparisons among eco-analytical laboratories, since samples of the majority of environmental objects is characterized by extremely low temporal stability.

In accordance with the Law on Ensuring the Unity of Measurements, the implementation of activities in the field of environmental protection falls within the scope of state regulation of ensuring the uniformity of measurements. Proceeding from this certified reference materials should be used for proficiency testing of laboratories performing water samples analysis. Specialists of UNIIM developed and produced on a permanent basis 14 types of certified reference materials (CRM) that simulating the composition of natural, drinking and waste water. A specimen of CRM the natural water’s mineral composition is a sample of a dry mechanical mixture of chemical substances designed to dissolve in a certain amount of distilled water. The CRM materials has a high degree of homogeneity and stability. The list of certified indicators of CRM is given in the table.

The main purpose of CRM of natural water’s mineral composition is external and interlaboratory control of measurement results accuracy, including proficiency testing. For laboratories that analyzed samples of water on mineral composition indicators, 15 different proficiency testing programs have been developed since 2000, including programs for measuring such indicators as COD, BOD and quality of biotesting. Virtually all CRM water’s mineral composition allows to estimate the measurement results accuracy for several composition indicators in one sample. Only in 2017 372 laboratories participated in interlaboratory comparisons conducted by UNIIM. The water composition components determined in the interlaboratory comparisons 2017 year included the main inorganic anions (nitrates, chlorides, fluorides, phosphates, sulfates and ammonium ions), individual elements (Ca, Mg, Na, K, Al, Fe, Mn, Pb, Cd, Cu, Zn, Cr), surfactants, suspended solids and a dry residue.

It should also be noted that all CRMs of natural water’s mineral composition have the property of metrological traceability to SI units: to kilogram and to cubic meter according to the CRM’s materials preparation procedures, to the unit mass fraction of the component through the using CRMs of initial chemicals for raw materials analysis. Due to this, positive results of participation in interlaboratory comparisons using CRM allows participating laboratories to declare the metrological traceability their measurement results.

T a b l e. - CRMs of natural water’s mineral composition produced by UNIIM

Registry number and index	Certified components
GSO 7886-2001 (МСВ А1)	Nitrates, fluorides, chlorides, sulfates
GSO 8124-2002 (МСВ К1)	Copper, lead zinc, cadmium
GSO 8938-2008 (МСВ АПАВ)	Chlorides, fluorides, phosphates, anionic surfactants
GSO 9450-2009 (МСВ Ж)	Calcium, magnesium, potassium, sodium, manganese, total hardness
GSO 9511-2009 (МСВ ХПК)	Nitrates, fluorides, chlorides, phosphates, chemical oxygen demand
GSO 9565-2010 (МСВ ПО)	Nitrates, fluorides, chlorides, phosphates, permanganate oxidability
GSO 9835-2011 (МСВ АК)	Nitrates, fluorides, chlorides, phosphates, sulfates, manganese, iron
GSO 9895-2011 (МСВ ВТ-Cr)	Chrome. For biotesting
GSO 10168-2012 (МСВ БПК)	Biological oxygen demand
GSO 10448-2014 (МСВ NH_4)	Ammonium, nitrates, fluorides, chlorides, phosphates, sulfates, iron
GSO 10815-2016 (МСВ М)	Nitrates, fluorides, chlorides, iron, turbidity
GSO 10912-2017 (МСВ В)	Nitrates, chlorides, phosphates, sulfates, iron, suspended solids
GSO 10917-2017 (МСВ AL)	Nitrates, chlorides, phosphates, iron, aluminum
GSO 11064-2018 (МСВ Щ)	Carbonates, Nitrates, chlorides, fluorides, sulfates, iron, manganese, total alkalinity

One of the main functions of the provider is to establish feedback from participating laboratories, including advisory services on program selection, evaluation of the quality of measurement results and analysis of possible reasons for obtaining measurement results, the accuracy of which is deemed doubtful or unsatisfactory. As practice shows, a joint discussion of the test results helps the participant laboratories to improve the accuracy of the measurements.

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DEVELOPMENT OF A CERTIFIED REFERENCE MATERIAL FOR DETERMINING TOTAL ALKALINITY OF NATURAL WATER

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Keywords: certified reference material, natural water, total alkalinity, titrimetric method of analysis, potentiometric titration, interlaboratory comparation, metrological traceability, accuracy control of measurement results

The alkalinity of drinking and natural water is a quantitative mark of water’s ability to react with hydrogen ions (protons). Hydroxide ions, anions of weak organic and inorganic acids, ammonia, amines and number of other substances are proton acceptors (substances of basic nature) in waters. Presence of hydroxide ions, carbonate ions and bicarbonate ions mainly causes alkalinity of drinking water and those natural waters that do not contain industrial pollutants. The alkalinity, due to total content of hydroxides, carbonates and hydrocarbonates, is called total alkalinity, is determined by visual or potentiometric titration by strong acid solution (usually hydrochloric) to pH 4,5 [1, 2] and is performed in mmol/dm^3.

According to [3] alkalinity of bottled drinking water should not exceed 6,5 mmol/dm^3. Increased alkalinity of drinking water leads to changes of human body acid-base balance. Control of alkalinity both of drinking and natural water is a necessary component of complex water researching by eco-analytical laboratories and laboratories of food industry enterprises, using water in production. Despite on comparative simplicity of total alkalinity measuring procedure, relative measurement results uncertainty for validated procedures [2, 4, 5, 6] ranges from 9 % to 28 %. Color and turbidity of water, present of free carbon dioxide, free chlorine, strong oxidants and reducing agents, weak volatile acids affect on total alkalinity measurement results.

Due to low time stability of drinking and natural water composition it is difficult to organize an external control of measurement results accuracy, including proficiency testing by interlaboratory comparisons, using of real water objects samples. In the Russian state register of approved types CRMs there is only one reference material for water total alkalinity (GSO 9285-2009), which presents a sodium carbonate aqueous solution. This sample is intended to calibration of measuring instruments used for determining of total alkalinity of water, but does not allow to estimate of alkalinity measurements results quality quite accurate, because its matrix is far from natural water composition.

In 2018 specialists of Ural Scientific and Research Institute for metrology (UNIIM) developed the certified reference material (МСВ ІІІ), imitating natural water’s mineral composition. The CRM is intended to control of measurement results accuracy of carbonate ions, nitrate ions, chloride ions, fluoride ions, sulfate ions, manganese, general iron contents and total alkalinity in drinking, natural waters and wastewater. The CRM may also be used for measurement procedures validation. The CRM material is a mechanical mixture of water-soluble mineral substances. Each sample presents the (250 ± 3) mg CRM’s material, which is intended to produce 1 dm3 of solution by dissolving in distilled carbon dioxide-free water. The composition of the solution is close to composition of natural chloride-sodium water with increased alkalinity. The requirements for the metrological characteristics of the CRM were established with considering measurement ranges and measurement results accuracy of the most common validated measurement procedures for CRM’s certified characteristics.

Industrially produced reagents were used as raw materials for the preparation of the CRM material. Solubility in water, absence of crystallization water in a substance composition, stability of substance composition, absence of interaction between substances after mixing in a dry form and after dissolution in water, stability of the material during storage, the color of obtained solution, and other factors affected on choice of reagents. For each reagent used as raw material for preparation of CRM basic substance mass fraction was measured according to validated measurement procedures, based on the method of visual titrimetry. Titrants correction coefficients were established using CRMs of the initial chemical substances: the CRM of sodium carbonate (GSO 4086-77), the CRM of sodium chloride (GSO 4391-88), the CRM of potassium dichromate (GSO 2215-81).

The raw materials were ground up to a particle size not more than 0,05 mm, dried at a temperature of (105 ± 2) °C to constant weight. Raw materials weighed portions were combined and thoroughly mixed in a stainless steel vessel by the “drunk barrel” method.

Manganese was chosen as a component-indicator for obtained CRM material homogeneity investigation. Following was taken into account for selecting a component-indicator:

1) When material of one CRM sample is dissolved in 1 dm^3 distilled water range of manganese mass concentration is from 0,025 mg/dm^3 to 0,100 mg/dm^3. In this case, the mass fraction of manganese in the CRM material is from 0,01 % to 0,04 %, this is much less than the mass fraction of each other components of CRM material.

2) All raw materials included in the composition of CRM have the same particle size.

3) Producer has ability to measure the mass concentration of manganese in a solution of CRM material by the atomic emission spectrometry method with inductively coupled plasma without additional sample preparation and carry out homogeneity investigation of CRM material close to repeatability conditions.

According with the technical specification on CRM the relative standard uncertainty value uh characterized CRM material homogeneity for manganese should not exceed 1,0 %. When this condition is fulfilled relative standard uncertainty from heterogeneity CRM material for all certified characteristics is taken to be 1,0 %. The value of uh is 0,96 % for first party of CRM.

Stability of total alkalinity certified value during the expected CRM shelf life (1 year) was proved by results of special experiment on first party CRM samples. Experimental data obtained during the year by potentiometric titration dissolved samples in accordance with [2] confirmed the stability CRM material.

The determination of CRM certified values and corresponding relative extended uncertainty values at k = 2 was carried out by a synthesis procedure in accordance with [7]. The certified value of total alkalinity was established by potentiometric titration to pH = 4,5 in accordance [2] with using the CRM of sodium carbonate (GSO 4086-77) for setting the hydrochloric acid titer. The metrological characteristics of CRM first batch are given in Table 1.

T a b l e 1. Metrological characteristics of first batch of the CRM MCB

Certified characteristic, measurement unit	The certified value	Relative extended uncertainty of certified value at k = 2, %
Mass concentration of carbonate ions (CO_3^{2-}), mg/dm^3	20,0	3,5
Mass concentration of nitrate ions (NO_3^-), mg/dm^3	20,0	3,5
Mass concentration of chloride ions (Cl^-), mg/dm^3	25,0	3,5
Mass concentration of fluoride ions (F^-), mg/dm^3	0,50	3,5
Mass concentration of sulfate ions (SO_4^{2-}), mg/dm^3	93,1	3,5

Certified characteristic, measurement unit	The certified value	Relative extended uncertainty of certified value at k = 2, %
Mass concentration of manganese, mg/dm^3	0,050	3,5
The mass concentration of total iron, mg/dm^3	0,200	3,5
Total alkalinity, mmol/dm^3	0,684	4,5

The CRM MCB ЩЦ has been included in Russian state register of approved types CRMs under the number GSO 11064-2018.

CRM first party samples was used in the interlaboratory comparison between seven accredited laboratories for determination natural waters total alkalinity and manganese and iron mass concentrations. The results of the interlaboratory comparison indicate good reproducibility mass concentrations of iron, manganese and total alkalinity certified values. The average values of participants measurements results deviate from the corresponding certified values by no more than 4,5 %, which confirms the practical applicability developed CRM.

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DEVELOPMENT OF REFERENCE MATERIALS IN THE LABORATORY MEDICINE. REFERENCE MATERIALS OF ELECTROLYTES IN THE BLOOD SERUM

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Keywords: electrolytes, serum, reference method, laboratory medicine, blood chemistry, traceability of measurements, atomic absorption lectern, atomic-emission analysis

The exchange of electrolytes is the most important part of the overall metabolism, aimed at maintaining the constancy of the internal environment of the body. Electrolytes are called salts, acids and bases, which in aqueous solution dissociate into positively charged cations and negative anions. The main cations of the body are sodium, potassium, calcium and magnesium; anions - chlorides, bicarbonate, phosphates and organic acids. [2],[3].

At the moment, there is a range of problems associated with the metrological provision of measuring instruments capable of determining the concentration of elements such as Ca, Mg, K, Na, etc.in blood serum. In routine measurements of electrolytes (salts, acids, bases, which in aqueous solution to a greater or lesser extent break down into free mobile ions) is mainly used potentiometric method. For potentiometric analysis of electrolytes (such as calcium, magnesium, potassium, magnesium, lithium, chlorine) in blood serum biochemical analyzers are used, having a potentiometric channel, or electrolyte analyzers. The principle of operation of such analyzers is based on ion - selective potentiometry. Tests of such measuring instruments for the purpose of entering into the state register of measuring instruments and their further verification are made with the help of certified reference materials of the defined element in water, however, the influence of the matrix on the accuracy of measurements is not excluded, and it is also necessary to take into account the error of preparation of aqueous electrolyte solutions.

Reference methods for determination of electrolytes in blood serum are [1]:

- Flame atomic absorption spectrometry;
- Flame atomic emission spectrometry;
- ICP - optical-emission spectrometry;
- Ion chromatography;
- ISP-mass spectrometry;
- Coulometry.

FSUE “VNIIOFI” has developed reference methods for determining the concentration of calcium, magnesium, sodium, potassium and lithium in blood serum, based on the methods that are reference in JCTML (Joint Committee for Traceability in Laboratory Medicine) [1],[4]:

- FR.1.31.0.06802 Reference method for measuring molar concentration of sodium in blood serum by atomic emission spectrometry with flame atomization;
- FR.1.31.0.06801 Reference method for measuring the molar concentration of potassium in blood serum by atomic emission spectrometry with flame atomization;
- FR.1.31.0.06800 Reference method for measuring the molar concentration of calcium in blood serum by atomic absorption spectrometry with flame atomization;
- FR.1.31.2010.09098 Reference methods of measurement of magnesium in serum;
- FR.1.31.2010 09096 Reference method for measuring the molar concentration of lithium in blood serum by atomic absorption spectrometry with flame atomization.

Currently the FSUE “VNIIOFI” are developing reference materials of electrolytes in the blood serum on the basis of the reference methods of measurement to ensure traceability of measurement analyzers, electrolytes of blood, including biochemical with ion-selective unit.

Tables 1 and 2 present the characteristics of reference materials of potassium, calcium and magnesium in blood serum obtained during the development process.

T a b l e 1. The range of mass concentration of the element, in g / dm^3 (mmol/dm^3)

index	Element		
	K	Ca	Mg
Level 1	0,126 (3,223)	0,102 (2,545)	0,017 (0,699)
Level 2	0,197 (5,039)	0,137 (3,418)	0,034 (1,399)

T a b l e 2. The expanded uncertainty of the certified values of reference materials, %

index	Element		
	K	Ca	Mg
Level 1	0,600	0,600	0,600
Level 2	0,604	0,600	0,600

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REFERENCE MATERIALS USED IN THE VETERINARY FIELD

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Keywords: reference material, drug, for veterinary use, monitoring, food safety, Customs Union

Over the last decades, the pharmaceutical industry has been experiencing intensive development, resulting in the expansion of the nomenclature of drugs for veterinary use and higher requirements for their quality and methods of control [1].

The use of drugs in violation of the instructions for their use, specifically, non-compliance with dosage, frequency and route of administration as well as non-respect of safe timing for using animal products often results in accumulation of residues of pharmacologically active substances in foodstuffs of animal origin, which, when used as food, pose a risk to the consumer and can also be one of the reasons for the emergence of antimicrobial resistance.

Ensuring the quality and safety of food products and medicinal products for veterinary use found in the consumer market and in circulation on the territory of the Russian Federation is a key task to be accomplished to raise living standards and improve the welfare of the population.

To achieve this, the Russian Federation authorities monitor food safety on the territory of the country, specifically, for drug residues, in compliance with the requirements of the technical regulations of the Customs Union (hereafter referred to as CU TR), and the efficacy and safety of medicinal products for veterinary use.

The fulfilment of these tasks require taking precise measurements in testing laboratories.

To carry out research, preference is given to sophisticated, selective, highly sensitive physical and physico-chemical methods of analysis which require use of reference materials of approved type [1, 3].

Use of reference materials (RM) is one of the key tools for ensuring cohesion, comparability and traceability of measurement results. Judging by the experience of recent years, domestic approved RM of pharmacologically active substances (DRM) are in high demand in laboratories of the Russian Federation, including laboratories of the Federal Service for Surveillance on Consumer Rights Protection and Human Wellbeing (“Rospotrebnadzor”), the Federal Service for Veterinary and Phytosanitary Surveillance (“Rosselkhoznadzor”), Standardization, Metrology and Testing Centres.

A list of reference materials found in the State Register of approved types of reference materials, when analyzed, shows a lack of a sufficient number of DRM, required, among others, for metrological support allowing to measure product safety indicators subject to technical regulations; indicators of composition and properties of materials subject to testing in the field of veterinary medicine, etc. [2].

In this connection, over the last few years, VGNKI has been developing the necessary nomenclature of domestic reference materials for antibacterial substances of approved type needed to provide metrological support allowing measurements of food and drug safety indicators.

According to the requirements laid down in GOST 8.315, VGNKI has developed seven reference materials for composition of antibacterial substances. They have passed the test procedure for type approval in compliance with the order and the procedure for type approval established by Order of the Ministry of Industry and Trade No. 1081 in conformity with the Administrative

Regulation on the provision by the Federal Agency for Technical Regulation and Metrology of a public service for approving the type of reference materials or that of measuring instruments.

With the need for reference materials in mind, VGNKI is carrying on with expanding the nomenclature of reference materials for antibacterial substances of approved type.

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MULTIPARAMETRIC REFERENCE MATERIALS REQUIRED FOR ANALYSIS OF GEOLOGICAL SAMPLES ON PRECIOUS METALS

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Keywords: precious metals, elemental and substantial analysis, geological samples, multiparametric certified reference materials of composition and properties

Elemental and material compositions, structure and size of mineral phases determine the physical and chemical properties of natural samples and man-made products. Variation of only one of these features can significantly change their consumer qualities. That is why the usage of multicomponent mixtures assumes the control of their composition and properties within processing of mineral raw materials, obtaining materials with desired properties, coatings application, etc. Often analytical control is carried out by physic-chemical and physic methods using regulated analytical techniques, in which certified reference materials (CRM) or reference materials (RM) are used for calibration of measuring instruments and quality control of results [1-5]. RMs to be adequate to the tested samples for composition or properties are used in the certification or verification of analytical techniques. Usually these are several sets of RMs or CRMs, one of which is used to determine the elemental composition, and the other is used to measure a specific property (the particle-size of a known phase composition, the particle-size distribution (PSD) in the mixture, the thickness of the layer, the electrical conductivity, the lifetime of mobile particles, etc.).

Methods of mineral raw materials, which include the determination of total content of precious metals (PM) in geological samples; species and particle size containing PM; description of the amount of particles containing PM and their PSD are widely used for geochemical and geological exploration, search and development of technology of enrichment of PM-ores. The data on mineral phases (species) of PMs and sizes of their particles in rocks, ores, and technological ore processing products are of paramount importance even if the total concentrations of precious metals slightly exceed average abundance in the Earth’s crust, because they allow the determination of mineral paragenesis accompanying ore mineralization processes and their use for the predictive assessment and revelation of ore bodies and the development and adaptation of separate steps of enrichment technologies in the variation of the composition of the initial ores for increasing the recovery of useful components.

In the last decades, automated mineralogy (MLA) has been used to solve the listed problems of mineralogical analysis [6-10]. The basis of different variants of this technology is scanning electron microscopy in combination with electron probe X-ray microanalysis, SEM–EPMA [11]. Mineralogical analysis based on of the scintillation atomic emission spectrometry (SAES) with the arc discharge has a better detection limits and does not require changing the aggregate state of the solid geological samples [12-14]. The SAES allows determining total concentrations of precious metals; the species of particles carrying PMs; as well as the sizes of these particles and their size distribution.

Technologies of automated mineralogy using SAES and SEM–EPMA provide: (1) measuring a large number of analytical signals from various elements of the sample in the optical, electronic and/or X-ray spectra in according to a certain scheme (under specified optimized conditions); (2) computer treatment of obtained multidimensional data by using heuristic techniques [15]. However,

both methods are relative. Therefore, single- and/or multiparametric RMs and CRMs are used for the initial setup of spectrometers and fulfilling analysis [16] at such steps as calibration of composition and size; experimental estimation of detection limits; correction of measured intensity of spectral lines and background on the matrix effects, spectral overlaps, instrumental noise, etc.; verification of mathematical models of knowledge or setting particle shape for stereological reconstruction of their sizes based on the measurements of analytical signals; quality control of the measurements of composition and size. Besides each of the methods has individual features of sample preparation for measurement. When interpreting information obtained about objects using MLA technologies based on fundamentally different analytical methods, these features should be taken into account [17-19].

The implementation and improvement of MLA technologies are associated with the simultaneous collection of diverse information on elemental and substantial compositions, as well as dimensional characteristics of mineral phases (PSD). The reliability of obtained results by MLA increases when training on multiparametric RMs and CRMs in which the required features of composition and properties are firmly established [16]. In this context, the term “multiparametric” implies not only the certification of the mass fractions of elements, but also the establishment of such characteristics as amount and size distribution of the particles of the individual mineral phases of precious metals, the granulometric distribution of the phases of each PM.

The currentness of creating multiparametric RMs for determination of precious metals in geological samples and usage in different analytical methods is beyond doubt. The difficulties of establishing certified metrological features of such reference materials are obvious and are associated with the lack of certified techniques, as well as a limited number of possible participants of the interlaboratory test. In general, there are no methodological approaches for developing and certifying of multiparametric reference materials of composition and properties for natural media.

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DEVELOPMENT OF CERTIFIED REFERENCE MATERIALS SET OF MAGNETIC PROPERTIES OF HARD MAGNETIC MATERIALS BASED ON NdFeB ALLOY

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Keywords: certified reference materials, remanent flux density, remanent magnetization, coercivity, hard magnetic material, State Primary Standard

Modern technological development of mankind is largely determined by the functional and structural properties of the used materials. A special place is occupied by magnetically hard materials. Based on magnetically hard materials products are sources of magnetic fields without expenditure of energy. High-precision magnetometric devices are required to control the magnetic properties permanent magnets, but tests of such measuring instruments is very difficult. Metrological assurance of the instruments is carried out mainly by the elementwise check of measuring instruments units. In this case, it is necessary to take into account the influencing factors: inhomogeneity of the magnetic field in the working area, the nonparallelism of the end faces of the pole pieces, the imperfection of the magnetic circuit, the magnetic viscosity of the material, and others and introduce appropriate corrections, which is practically an impossible task. The most effective way to solve this problem is to develop certified reference materials of magnetic properties of magnetically-hard materials.

Permanent magnets based on the neodymium-iron-boron alloy (NdFeB) are one of the most popular in practice. For this reason, sintered permanent magnets of NdFeB type were chosen for research and further development of reference materials. The research and development of the reference materials was carried out at Ural Research Institute for Metrology in 2017-2018.

Certified reference materials of magnetic properties of permanent magnets based on Nd-Fe-B alloy (set of NdFeB) were approved. The interval of the allowed certified values was established, the errors and uncertainties of the certified values were determined, the expiration date of reference materials was determined. The first batch of reference materials was produced. The developed set of certified reference materials received the numbers of GSO 11059-2018 / GSO 11062-2018 in the State Information Fund.

Reference materials are cylinders of NdFeB alloy obtained by pressing an alloy powder in a magnetic field, followed by sintering in a vacuum or an inert gas environment. For consumer convenience, reference materials are designed as a set of materials with different diameters. The nominal length of the reference material is 10 mm, the nominal diameters are 7, 12, 22, and 36 mm. Reference materials are reinforced with an outer ring made of paramagnetic material of the same height as the reference material to prevent their destruction.

Establishment of certified reference materials magnetic values were carried out using the State primary standard GET 198-2017 [1]. Values of normalized metrological characteristics are given in Table 1.

T a b l e 1.Normalized metrological characteristics

Index in the SRM	Characteristic	Certified value range	Allowed values limits of the relative error of the certified value (P=0,95), ± δ, %	Expanded uncertainty of the certified value (P=0,95, k=2), %
MC NdFeB-7	Remanent flux density, B_r, T	от 0,900 до 1,500	2	2
MC NdFeB-12		от 0,900 до 1,500	2	2
MC NdFeB-22		от 0,900 до 1,500	2	2
MC NdFeB-36		от 0,900 до 1,500	2	2
MC NdFeB-7	Remanent magnetization, M_r, kA/m	от 715,0 до 1200,0	2	2
MC NdFeB-12		от 715,0 до 1200,0	2	2
MC NdFeB-22		от 715,0 до 1200,0	2	2
MC NdFeB-36		от 715,0 до 1200,0	2	2
MC NdFeB-7	Coercivity H_{cB}, kA/m	от 680,0 до 990,0	3	3
MC NdFeB-12		от 680,0 до 990,0	3	3
MC NdFeB-22		от 680,0 до 990,0	3	3
MC NdFeB-36		от 680,0 до 990,0	3	3
MC NdFeB-7	Coercivity H_{cM}, kA/m	от 800,0 до 3500,0	3	3
MC NdFeB-12		от 800,0 до 3500,0	3	3
MC NdFeB-22		от 800,0 до 3500,0	3	3
MC NdFeB-36		от 800,0 до 3500,0	3	3
MC NdFeB-7	Maximum energy product, $(BH)_{max}$, kJ/m^3	от 150,0 до 400,0	4	4
MC NdFeB-12		от 150,0 до 400,0	4	4
MC NdFeB-22		от 150,0 до 400,0	4	4
MC NdFeB-36		от 150,0 до 400,0	4	4

In view of the high demand for permanent magnets of the SmCo type it is planned to develop and approve a new set of certified reference materials of permanent magnets based on corresponding magnetic materials in 2018.

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MULTIPARAMETRIC CERTIFIED REFERENCE MATERIALS USED FOR METROLOGICAL SUPPORT OF COATING PARAMETERS

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Keywords: reference materials, coatings, error, uncertainty

There is a tendency to create devices that allow analyzing multilayer two and three-component coatings, to measure the thickness and surface density of coatings simultaneously, as well as the chemical composition of the coating in the last years [1].

UNIIM has been working for 40 years to improve metrological support for measurements of surface density and coating thickness based on XRF and back-scattered beta radiation methods. Now this type of measurement has been determined as independent with its own measurement chain [2], which establishes the order for calibration of XRF thickness gauge and surface density meters using the state primary standard [3].

The most common XRF method allows measuring the chemical composition, including multicomponent and multilayer coatings in the range from 10 nm to 50 μm with high measurement locality (up to 0.01 mm^2). Modern XRF surface density meters and thickness gauges have wide measurement capabilities including the ability to measure the chemical composition of multicomponent and multilayer (up to 24 layers) coatings [4].

Two types of reference materials of surface density, thickness and mass fraction of elements in the coating were certified:

- CRM coated with nickel-iron alloy on silicon (GSO 10880-2017)
- CRM coated with nickel-iron-cobalt alloy on silicon.

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ON THE DEVELOPMENT OF CERTIFIED REFERENCE MATERIALS FOR MELTING POINT OF HIGH-PURITY ORGANIC SUBSTANCES

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Keywords: reference materials, melting point, purity, cryometric method

The field of the melting point measurements now includes numerous lab equipment items that are used in medicine, biology and cosmetics industry.

Most of the commercial units that are used for determination of melting point of organic substances have measurement range from room temperature to 350 – 400 °C, considering that for pharmaceutical and medical industry the range from room temperature to 250 °C is of the most practical importance. The uncertainty of measurement in that range for measuring equipment of foreign manufacture is of 0,3 – 0,5 C.

For calibration of measuring equipment in this field three imported CRM types are currently used, which are based on benzophenone, caffeine and benzoic acid in the melting point range from 47,6 to 237,0 °C. Worldwide the selection of melting point CRMs is wider, but metrological characteristics of CRMs manufactured by different producers are quite similar and do not exceed the characteristics of the already imported CRMs, therefore the foreign-made CRMs still don't fully satisfy the demand of Russian pharmaceutical industry. Therefore the current research at Calorimetric Laboratory of VNIIM is focused on the development of such locally produced CRMs.

The primary objective of the conducted research is to create several melting point CRMs of high-purity organic substances in the range of melting point values from room temperature to +250 °C, and the uncertainty not exceeding 0,1 °C, in order to satisfy for the near future the demands of the industry for the range and accuracy of the measurements.

To achieve this goal two approaches are being explored. To implement the first one a unit consisting of a dry-well calibrator, a precision multimeter and a platinum resistance thermometer (100 Ω), calibrated according to [1], was set up.

The second approach involves using cryometric measuring complex Krian. The cryometric method has been accepted as a primary measurement method by Consultative Committee for Amount of Substance - Metrology in Chemistry and Biology - Bureau International des Poids et Mesures (CCQM BIPM) and has been used for many years in the laboratory for characterization of the purity of K-3 and K-1 benzoic acid. As it is based on obtaining the melting curve of the substance, it is possible to simultaneously determine both purity and melting point values.

For the purity determination the sources of uncertainty were thoroughly analyzed and their influence was significantly lowered [2]. The uncertainty of the melting point is currently being investigated using several substances with the melting point within Krian's measurement range from 40 to 250 °C. In order to select the substances, the set of requirements for them was established: chemical stability, melting without decomposition, low volatility, non-toxicity and possibility of obtaining the substance with sufficient degree of purity were taken into account. Considering those requirements, anthracene, benzoic acid, benzophenone, caffeine, vanillin and nicotinic acid were chosen for the research.

Besides that, basing on the construction and basic principle of Krian’s measurement cell, steps were made to renew its hardware and software system, and these changes allow us to expect to achieve higher precision.

Overall, the instrumental basis for the development of melting point certified reference materials of high-purity organic substances has been set, and further research will be focused on obtaining experimental data and estimating the uncertainty.

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PROBLEM OF COMPARABILITY OF CHARACTERISTICS OF CERTIFIED REFERENCE MATERIALS – GAS MIXTURES OF THE SAME KIND, PRODUCED BY DIFFERENT ENTERPRISES

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Keywords: metrology, certified reference material, gas mixture, State primary measurement standard, secondary measurement standard, working measurement standard, traceability, quality control

In accordance with GOST 8.578-2014 “GSI State hierarchy scheme for measuring instruments of the content of components in gaseous mediums” [1], gas certified reference materials in cylinders under pressure (hereinafter referred to as reference materials) are working standards and act as material measures for measuring instruments of the content of components in gaseous mediums, by means of which tests, verification, calibration of measuring instruments are carried out. The mass application of reference materials in the production and control of measuring instruments is confirmed by the annual release of about 100 thousand cylinders with gas mixtures in the status of certified reference materials in Russia.

At present, quality control of produced material measures of any physical magnitude is provided in accordance with the current regulatory and legislative framework:

- through testing for type approval purposes and entering into the Federal Information Fund to ensure the uniformity of measurements,

- through the primary mandatory verification of material measures during the release from production and periodic mandatory verification of material measures by the accredited body in accordance with Federal Law No. 412-FZ of December 28, 2013 “On Accreditation in the National Accreditation System” [2].

For reference materials acting as material measures for measuring instruments [1, 3], these requirements do not apply. At present, all reference materials pass only the test procedure for type approval and entry into the Federal Information Fund to ensure the uniformity of measurements [4]. When releasing from production and then when applying them, there are no compulsory procedures for reference materials similar to the procedures for verificating material measures.

This discrepancy in regulatory and legislative acts has existed for many years and there have been no serious attempts to change the legislation in the field of metrology by providing uniform order for material measures and reference materials.

Considering that reference materials are used for calibration and verification of measuring instruments used for monitoring sanitary, ecological, industrial safety, quality control of hydrocarbon products, etc., the issue of ensuring the quality of industrially produced reference materials becomes important.

At present, there are 20 enterprises operating on the territory of the Russian Federation, which, in effect, constitute a special branch for the industrial production of gas certified reference materials. Ensuring compliance of metrological characteristics of released reference materials with the established requirements [1], including ensuring for one consumer the comparability of reference materials, which can be attributed to gas mixtures of the same kind, produced by different enterprises of the branch, is a very important task.

To solve this task it is proposed to use some criterions based on study of random errors of certification of reference materials either on one enterprise or all enterprises producing reference materials at Russian Federation [5].

Development and implementation of these criterions would optimize the reference material’s certification procedure and improve the quality of such product for Russian consumers. It would also optimize the quality control of enterprises producing reference materials carring out by State primary measurement standard.

Taking into account that the whole nomenclature of produced reference materials in the amount of 100 thousand cylinders is more than 10 thousand kinds of gas mixtures that are characterized by different component composition of the mixture, different quantitative characteristics of the content of each component in the mixture, the tolerance for the preparation of each component, the values of the expanded uncertainty of the contents of each component in the mixture, it is impossible to carry out quality control of enterprises on all kinds of gas mixtures.

It is therefore proposed to distinguish about 20 representative groups from the whole set of kind of gas mixtures, formed on the basis of the following principles:

- application of the same type of universal means for the preparation and analysis of gas mixtures;

- use of the same type of cylinders, valves and other gas fittings;

- the use of the same type of methods for the preparation of cylinders for gas mixtures based on reactive gases, inert, constant gases, microconcentrations of the components to be determined, etc.

This approach is discussed at the level of the Consultative Committee for Amount of Substance of the International Bureau of Weights and Measures in the Working Group on Gas Analysis, which proposes to separate a number of gases and gas mixtures based on them into one so-called “flexible” group (flexible gases). The results of constant participation in the comparisons of one gas from the “flexible” group can be extended to other gases from this group and, thus, to confirm the calibration and measurement capabilities for all gases from the “flexible” group. It should be borne in mind that the degree of standardization of primary methods of preparation and analysis of mixtures, training of cylinders, etc. much higher abroad, compared with the methods implemented at the enterprises of the Russian Federation.

Only integrated approach to quality assurance of industrially produced reference materials, including optimization of reference materials certification procedure in every enterprise, optimization of quality control procedure by authorized facilities, implementation of ISO 17034 quality management system in enterprises, will lead to improvement of the professional skills of enterprises and ensure the compliance of reference materials with the high modern requirements in traceability and accuracy.

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ON CALIBRATION AND MEASUREMENT CAPABILITIES OF COOMET NATIONAL METROLOGICAL INSTITUTES IN THE FIELD OF PHYSICAL AND CHEMICAL MEASUREMENTS

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Keywords: national metrological institute, regional metrology organization, key comparison, amount of substance, BIPM database, measurement category, calibration and measurement capabilities, reference material

Regional metrology organizations (RMOs) are one of the key elements for the global metrological system. RMOs activities provide conditions for mutual recognition of measurement results of National Metrology Institutes (NMIs), which are signatories of the CIPM Mutual Recognition Arrangement (CIPM MRA), if its provisions are respected. NMIs of the Member States participate in the CIPM MRA through their RMOs only.

COOMET is an organization for cooperation of National Metrology Institutes from Central and Eastern Europe and Asia countries. At present, 42 NMIs from 21 countries are COOMET Members, including 5 Associated Members, which are Full Members of other Regional metrology organizations.

COOMET Technical Committee TC 1.8 “Physical Chemistry” provides activities in the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) field of work. TC 1.8 “Physical Chemistry” work is primarily related to implementation of the CIPM MRA through the following activities:

– planning and organization of international comparisons and interlaboratory research,

– organization and provision of intra-regional and inter-regional peer review of Calibration and Measurement Capabilities (CMC) of the COOMET NMIs,

– involvement of COOMET experts in inter-regional peer review of CMC of NMIs from other RMOs.

TC 1.8 “Physical Chemistry” is one of the most active regional Technical Committees in the field of metrology in chemistry and biology, which is reflected in the number of Key Comparisons COOMET NMIs participate in. COOMET NMIs participate in virtually every comparison under the auspices of the CCQM in the field of gas analysis and electrochemistry.

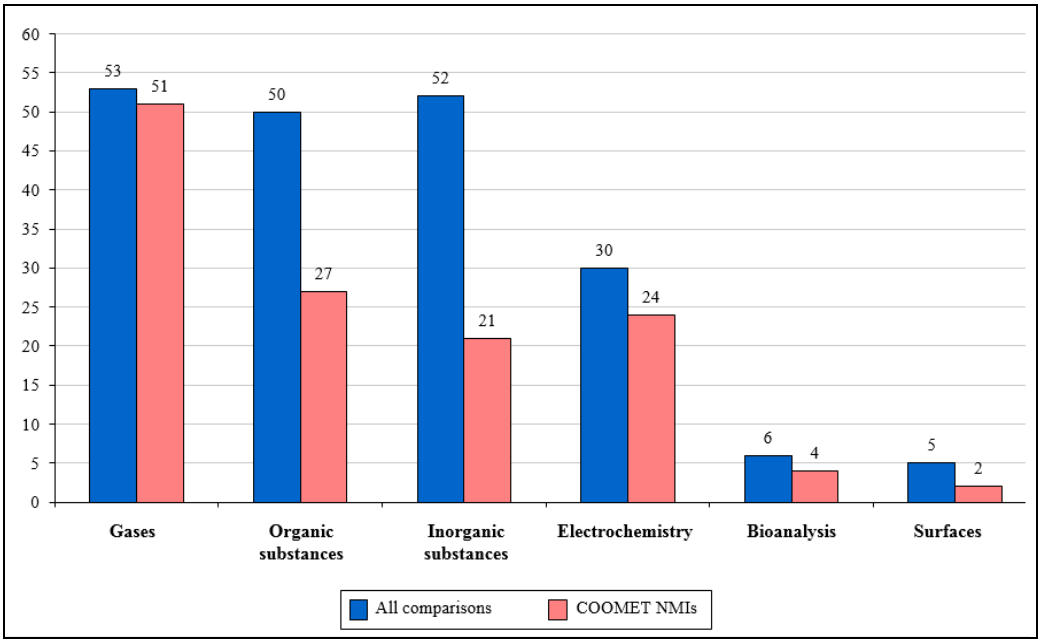

Fig. 1. Activity of COOMET NMIs in CCQM Key Comparisons

Key Comparisons conducted by RMOs are related to the International Committee for Weights and Measures (CIPM) Key Comparisons through the NMIs that represent RMOs. A degree of equivalence established in the course of a RMO Key Comparison has the same status as degree of equivalence established in the course of a CIPM Key Comparison.

The result of Key Comparisons conducted are the Calibration and Measurement Capabilities registered in the key comparison database maintained by the International Bureau of Weights and Measures (BIPM KCDB). Calibration and Measurement Capabilities of the NMIs that declare their CMC through COOMET are as follows: VNIIM – 591 CMC, UNIIM – 30 CMC, VNIIFTRI – 11 CMC, Ukrmetrteststandart – 35 CMC, BelGIM – 19 CMC, KazInMetr – 7 CMC. Number of CMC for measurement categories in accordance with the CCQM classification is shown in Fig. 2.

Gases	512
Organic solutions	24
Inorganic solutions	15
Metal and metal alloys	14
Sediments, soils, ores, and particulates	21
Biological fluids and materials	4
High purity chemicals	36
Food	8
Water	12
Advanced materials	20
Electrochemical analysis	24
Other materials	3

Fig 2. Number of CMC for measurement categories in accordance with the CCQM classification

The feature of the CMC in the field of metrology in chemistry and biology is that KCDB BIPM also includes information on Reference Materials (transfer measurement standards) produced by NMIs on a regular basis.

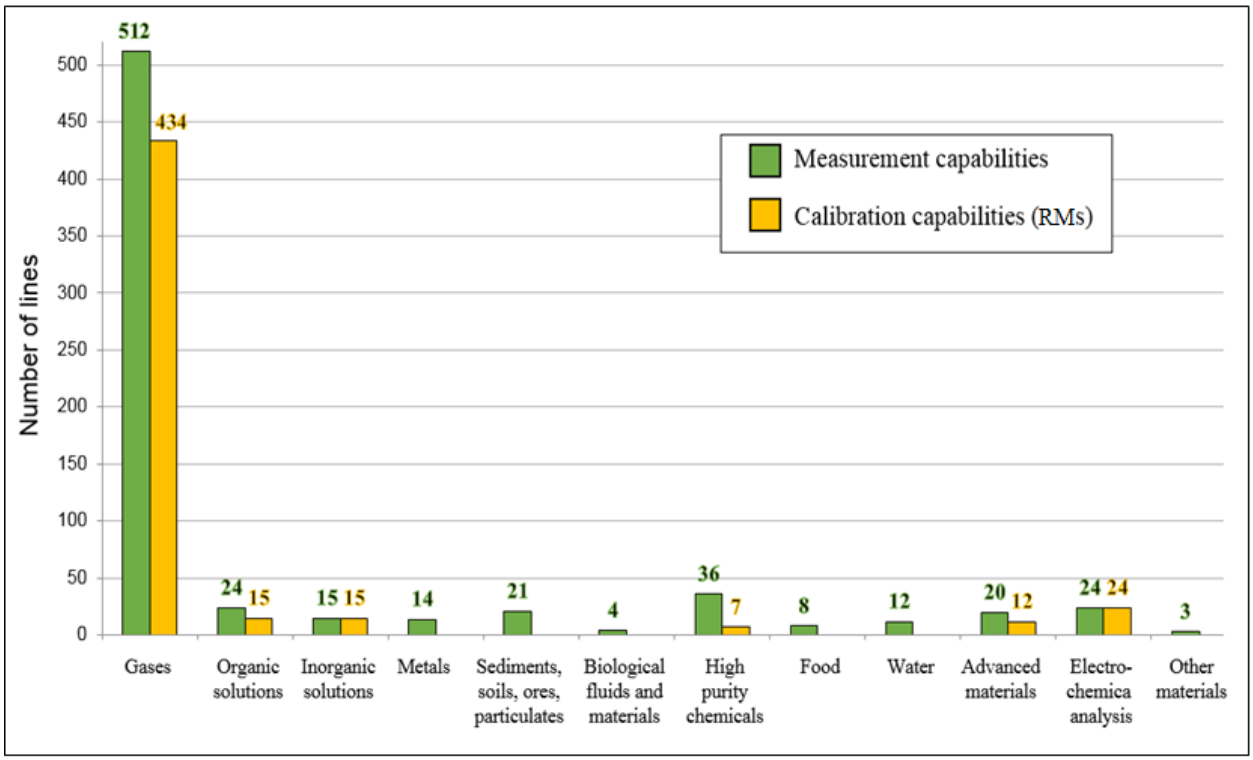

Fig. 3. Measurement/Calibration (RMs) capabilities of COOMET NMIs by categories

An important indicator of RMOs activity is growth dynamics of COOMET NMIs' CMC and emerging of CMC in new measurement categories. During the last 6 years of COOMET activity, level of CMC significantly increased in relation to CMC of NMIs, which are the world leaders in such measurement categories as *High Purity Chemicals*, *Water*, *Advanced Materials*, *Sediments and Soils*; new CMC emerged in the *Biological Fluids and Materials* measuring category. The results achieved allow comparisons for various measurement categories in such areas as ecology, medicine, energy, food, and material properties within the framework of COOMET.

Over the long term, it is necessary to solve issues of importance related to ensuring the reliability of measurement results of gas content in transformer oil, mercury content in natural gas, carbon isotopes ratio in ambient air carbon dioxide and methane, dioxide content in ash dust and other matrices.

Rich area of activity and Key Comparison results allow COOMET TC 1.8 "Physical Chemistry" to take rightful place among specialized Technical Committees of other RMOs.

REFERENCE MATERIALS TO ASSESS SPECIFIC SAFETY OF PREPARATIONS OF IMMUNOGLOBULINS, AND HUMAN ALBUMIN: DEVELOPMENT, VALIDATION AND APPLICATION

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Keywords: quality examination, human immunoglobulin preparations, human albumin preparations, specific safety, anticomplementary activity, anti-A and anti-B haemagglutinins, anti-D antibodies, prekallikrein activator, reference materials, haemagglutination methods, complement binding test, chromogenic method

High requirements for specific safety associated with the effect of the drug on the complement system, kallikrein-kinin and haemostasis are imposed on human immunoglobulin (IGH) and human albumin (AH) infusion drugs. The presence of haemagglutinins (HAG) (anti-A and anti-B antibodies - immunoglobulins G) in the titer less than 1:64 reduces the risk of extravascular adverse reactions caused by the activation of macrophages in the first 10 days after intravenous administration of IGH in patients not I(0) blood group. When the content of anti-D antibodies in this preparation, the titer of not more than 1:8 in Rh-positive patients with immune system disorders, the probability of hemolytic complications of immunoglobulinemia insignificant. Anti-complementary activity (AKA) no more than 50 % (which corresponds to no more than 1 CH_{50} per 1 mg of immunoglobulin protein) allows to eliminate such undesirable reactions as tides, headache, fever, tachycardia. When the content of the activator prekallikrein (APK) for infusion drugs, IGH and AH less than 35 IU/ml anti-hypertensive effect associated with the effect on the kallikrein-kinin system in the infusion, are minimal. “Anti-A and anti-B haemagglutinins”, “Anti-D antibodies”, “Anti-complementary activity ”, “Prekallikrein activator ” - quality indicators that allow to predict the tolerability of patients using these drugs. Methods of evaluation based on biological effects (agglutination or hemolysis of red blood cells), amidolytic properties of the products of the cascade reactions (cleavage of specific substrate) and involve the use of reagents of biological origin (complement, hemolytic serum, red blood cells antiglobulin serum, prekallikrein), the standard of which all the properties are impossible. However, the modern practice of drug expertise imposes increasingly stringent requirements to the methods and techniques used in the evaluation of the quality of drugs. Of fundamental importance in the improvement of testing procedures of drugs, IGH and AH indicators have specific safety reference materials (RMs), some of which are used to assess the stability of the analytical work (assessment of suitability of the system) in the application of methods of determination AKA, the determination of the content of HAG or anti-D antibodies, together with other methods of testing are a means of transferring the unit size and allow us to establish the quantitative content of HAG, anti-D antibody, APK [1]. With the aim of standardizing methodologies for the assessment of specific drug safety IGH and AH were developed and included in the Russia State Pharmacopoeia 13 (XIII) of the General Pharmacopoeia Monograph (CFM) “Determination of anticomplementary activity of medicinal products containing human immunoglobulins”, “Determination of anti-A and anti-B haemagglutinins in medicinal products containing human immunoglobulins”, “Test for anti-D antibodies in medicinal products containing human immunoglobulins” [2].

Methodology for determining AKA in accordance with the CFM.1.8.2.0007.15 the use of RMs is provided, the positive and negative controls of which allow to evaluate the stability of the

analytical work in different ranges of test results. Currently, in international practice is used RMs, approved by the European Directorate for Quality of Medicines and Health (EDQM). Human immunoglobulin for anticomplementary activity of BRP, which is a highly purified, freeze-dried IGH [3]. To obtain values in the range of more than 50 % (positive control), the instructions for its use provide for an increase in the amount of the initial reduced solution of RM to 0.8 ml when using 0.2 ml for negative control. The certified values of AKA of this RM are in a wide range and regardless of the series are 10-40 % and 60-100% for negative and positive controls, respectively. Domestic RM human immunoglobulin (ISS 42-28-430) consists of two components: negative control - solution of IGH with an average value of AKA 40.5; 41.6 and 38.7 % (for the three certified series), positive control – solution heat-treated, IGH with the average value AKA 76,6; 75,7 and 69,9 % [4]. The established uncertainty from these series was no more than 10 %.

The number of anti-A and anti-B HAG in immunoglobulin preparations can be detected by direct (MDG) and indirect hemagglutination (MINDG) [5]. Their titer is defined as the maximum dilution of the drug, in which agglutination of test erythrocytes of any intensity occurs. To control the stability of analytical work in different ranges of values of the results of determining the content of HAG, it is necessary to use positive and negative RMs. To estimate the quantitative RMs with the HAG content in the titer 1: 64 (with the RM content limit), equal to the maximum permissible for the studied drugs. The content of anti-A and anti-B HAG in the blood of donors is not the same, that in the development of positive RM predetermines the need to use different approaches. Thus, the positive control in the composition of the international RMs (NIBSC) is a solution of IGH with different HAG content: anti-A in the range from 1:32 to 1:64, anti-B – from 1:16 to 1:32 [6]. RM EDQM, also being a solution of IGH, contains both anti-A and anti-B hemagglutinins at the level of 1:32 [3]. RM limit of HAG EDQM and NIBSC are IGH solutions with the addition of mouse monoclonal antibodies to achieve the target value of 1:64. These RMs are certified and recommended for use only in the MDG. Given the acceptability of the use for quality control of drugs, IGH the HAG content of the two methods developed by domestic, RMs “Kit for determination of the content of anti-A and anti-haemagglutinin” (ISS 42-28-439), which includes five components [7]. Four of them are made from the plasma of blood donors I(0) groups and have the certified value of the content of anti-A or anti-B using the MDG and MINDG. The negative component does not contain HAG due to the use of blood plasma of donors of VI(AB) group. The presence of RMs, certified characteristics of which are established with the use of MDG and MINDG, allows to standardize these methods, as well as to conduct a comparative assessment of the quantitative characteristics of HAG impurities in various IGH preparations.

In accordance with CFM.1.8.2.0004.15 the anti-D antibody content of IGH preparations determined in the haemagglutination reaction shall not exceed the titer of the positive standard. Titer of anti-D antibodies is defined as the maximum dilution of the drug, in which the agglutination of Rh-positive red blood cells of any intensity. The specificity of the analysis is confirmed by the use of negative RM and Rh-negative erythrocytes. Currently, in international practice, they are used RM NIBSC and EDQM [3,6]. Positive RM has a nominal titer of 1:8 and was obtained by reconstituted 2nd International Standard for anti-D immunoglobulin (with an activity of 285 IU/ml) at 1/6000 dilution in IGH. RM the domestic “Kit for determination of the content of anti-D antibodies” (ISS 42-28-440-2017) includes two components [8]. The negative component, made from blood plasma of Rh-positive donors of I(0) blood group, does not contain anti-D antibodies. The target value of the anti-D antibodies content in the positive component is achieved through the use of blood plasma Rh-negative donors of IV(AB) blood group. The positive component was certified by two

methods: haemagglutination (titer is 1: 8) and flow cytometry (antiresus activity is 0.7 IU/ml). The presence of characteristics certified in comparison with international methods with two, one of which (flow cytometry) is more accurate and objective, allows to standardize the production of a positive component of RM.

The assessment of the limit content APK is carried out by chromogenic method by comparison with RM calibrated in ME [5]. Modern RMs are a series of drug AH with a high content APK, approaching the maximum allowable in the formulations of IGH and AH, which can be achieved by modifying certain stages of the manufacturing technology of the drug (EDQM, NIBSC) or making advanced, high-purity APK (USP) [3,6,9].

Thus, reference materials play a key role in the assessment of specific safety of human immunoglobulins and albumin. Development of RMs, which are the carrier of the quantitative characteristics of impurities of drugs, causing the occurrence of adverse reactions in their application, requires the selection of a candidate for RMs. Domestic RMs are developed taking into account the maximum approach to the true content of impurities in their composition, the quantitative characteristic of which is the certified value. Due to the lack of currently alternative methods for measuring the values characterizing the indicators of specific safety, ISS “Human immunoglobulin”, ISS “Kit for determining the content of anti-A and anti-B haemagglutinins” are certified by the same technique for which they are intended. The advantage of the positive component of the ISS” Kit for determination of the content of anti-D antibodies” is the certification of its two methods.

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METROLOGICAL SUPPORT OF GAS ADSORPTION ANALYSIS

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Keywords: reference material, adsorption analysis, state primary measurement standard

For today the state primary measurement standard of units for specific adsorption of gases, specific surface area, specific volume and diameter of pores of solids and materials (GET 210-2014) is created on the basis of UNIIM. The gas adsorption (volume) method of low-temperature gas adsorption, which is recognized internationally as highly accurate, is based on the measurement standard.

To achieve unity and required accuracy of measurement in the gas adsorption analysis it is necessary to transfer units of specific adsorption of gases, specific surface area, specific volume and diameter of pores to working measurement standards and measurement instruments of then above listed characteristics.

According to the project of State verification scheme for measurment instruments of specific adsorption of gases, specific surface area, specific volume and diameter of pores, transfer of sorption characteristics to working measurement standards and measurement instruments is carried out through reference materials of the approved type of sorption characteristics, the intervals of certified values are given in Table 1:

T a b l e 1. Name of sorption characteristics, intervals of acceptable certified values and bounds of acceptable values of relative errors

Name of sorption characteristics	Intervals of acceptable certified values	Bounds of relative error of RM certified value for P=0,95, %
Specific surface area	from 0,10 to 2500 m^2/g	±4
Specific volume of pores	from 0,05 to 2,00 cm^3/g	±4
Average (prevailing) diameter of pores	from 0,5 to 100 nm	±10

At present in the Russian Federation the following reference materials are used for ensuring the uniformity of measurements of sorption characteristics. (Table 2).

Previously, in the territory of the Russian Federation to transfer units of sorption characteristics high-priced foreign reference materials of BAM (Germany), NIST (USA), BCR (Belgium) were used, period of validity of type approval certificates of these reference materials has expired, therefore the use of these reference materials according to the current legislation is impossible.

Based on the analysis of the register of reference materials of sorption characteristics and comparison of the results of the analysis with the data of Table 1, it can be said that valid reference materials of an approved type cover a wide range of non-porous, microporous and mesoporous solids and materials. These reference materials allow to test measurement instruments of sorption characteristics, and are intended for certification and control of accuracy of measurement methodologies for sorption characteristics, can be used for verification, calibration of measurement instruments, testing of measurement instruments used to control the quality of nanoindustry products, catalysts, membranes and filters for cleaning gas and liquid media from various types of pollution.

T a b l e 2. Summary table of reference materials of an approved type.

Name of RM	Certified characteristic	Interval of permissible certified values	Bounds of permissible values of relative error for P=0,95, %	Relative uncertainty for k=2, %
GSO 10449-2014 RM of nanoporous alumina oxide (Al_2O_3 UNIIM RM)	Specific surface area (BET) S, m^2/g	from 100 to 300	± 2,0	2,0
	Specific volume of pores V, cm^3/g	from 0,2 to 1,0	± 3,0	3,0
	Average diameter of pores 4V/S, nm	from 5 to 20	± 3,0	3,0
GSO 10734-2015 RM for sorption properties of nanoporous zeolite (Zeolite UNIIM RM))	Specific surface area, m^2/g	from 500 to 1200	± 3,0	3,0
	Specific volume of pores, cm^3/g	from 0,1 to 0,5	± 3,0	3,0
	Prevailing diameter of pores, nm	from 0,4 to 0,9	± 3,0	3,0
GSO 10735-2015 RM for sorption properties of nanoporous corbon (S RM UNIIM))	Specific surface area, m^2/g	from 30 to 60	± 4	4
	Specific volume of pores, cm^3/g	from 0,1 to 0,5	± 10	10
	Average diameter of pores, nm	from 10 to 20	± 10	10
GSO 10900-2017 RM for specific surface area of quartz sand ($QSiO_2$ UNIIM RM))	Specific surface area, m^2/g	from 0,2 to 1,0	± 4	4

In case of consumer demand, and also if it is necessary to carry out tests or calibration of measuring instruments, that implement gas adoption analysis, using reference materials different in nature and chemical composition from reference material of approved type (quartz sand, zeolite, aluminum oxide), it is possible to develop reference materials of sorption characteristics, on the basis of solid porous oxides or natural minerals.

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APPLICATION OF RAMAN SPECTROSCOPY WITH THE PURPOSE OF DRUGS QUALITY CONTROL IN INJECTION FORM

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Keywords: Raman spectroscopy, identity and confirmation of authenticity of medicines, attestation of measurement procedures

To preserve the life and health of people, the quality of medicines used for their treatment is very important. One of the main conditions for ensuring the quality of medicines is the identification or confirmation of the authenticity, as well as the control of the content of the basic component.

Analysis of current trends in the development of new methods of analysis in medicine shows that in the vast majority of cases on the first place today are methods that minimize the analysis time, the destruction of medications. In this case, the method of Raman spectroscopy in carrying out routine measurements has these advantages over traditional methods of wet chemistry, especially for drugs in injection form, because it is non-destructive, contactless, express method and it does not require sample preparation [1].

The purposes of current work are development and attestation of procedure of identity and following quantity determination of basic components content by means of Raman spectroscopy for the drugs in injection form and confirmation of measurement procedure characteristics by means of proficiency testing schemes realization.

The work was carried out by FGUP "UNIIM", Ekaterinburg in conjunction with FGBU "IMCEAATMA" Roszdravnadzor, department for the development of non-destructive methods of testing the quality of medicines, Kazan.

Measurement procedure of identification or confirmation of authenticity is qualitative measurement technique. The identification of drugs is carried out by comparing the Raman spectra of the test sample, with similar spectra obtained from the original medications previously and stored in the database.

There are no currently requirements for the development, documentation and legalization of qualitative measurement procedure therefore for the estimation of accuracy indices of measurement procedure quantitative characteristic has been used in the form of a correlation coefficient between the measured and library spectra in the range from 0 to 1.

Accuracy indicators has been evaluated in the form of precision indicators, which has been calculated in accordance with [2] from the data of a quasi-laboratory experiment involving five laboratories. Metrological characteristics are given in Table 1.

The quantitative measurement procedure the contents of basic components in injectable drugs using the Raman method is based on a directly proportional relationship of the intensity (I) of the spectral lines to the number of molecules (N) per unit volume:

$$I = i \cdot k \cdot N \quad , (1)$$

where i – intensity of scattered light per molecule; k – coefficient, depending on the experimental conditions, (coefficient constant for used measuring instrument.

During the attestation of measurement procedure the following medicines have been used as sample for estimation: ascorbic acid, novocaine and sodium thiosulfate that have been analysed on the State secondary standard of mass fraction, mass (molar) concentration of components in solid and liquid substances and materials based on volumetric titration method GVET 176-1-2010 (hareafter - GVET 176-1-2010).

The usage of GVET 176-1-2010, which confirmed its calibration and measurement capabilities through participation in international key comparisons CCQM-K130 [3] and CCQM-K149 [4], provides a modern requirement for traceability of measurement results to SI units [5].

The estimation of accuracy indices has been carried out in accordance with [2]. The estimation of the correctness factor was carried out by estimating the bias of the measurement results obtained at GVET 176-1 2010 and the results obtained using the measurement procedure that is evaluating. In addition, a multifactorial experiment has been conducted to evaluate the influence of methodological factors on the results of measurements [6]. Factors studied: ambient temperature, packaging option (volume of the ampoule), manufacturers, content of the main component, solvents. The data was processed by means of regression analysis using the Microsoft Excel package.

During the treatment of date of multifactor experiment, the following shift value was obtained? for instance, for novocaine:

$$\Delta П = 1,010(\mathrm{C} - C_0) - 0,005(V - V_0) + 0,0001(S - S_0) + 1,320(P - P_0) + 0,092(T - T_0) \quad , (2)$$

Thus, the influence of the methodological parameters has been calculated from the formula:

$$\sum_{\xi=1}^{P}\left(\frac{\partial C_i}{\partial \Delta П_\xi}\right)^2 \cdot \Delta^2(\Delta П_\xi) = \sqrt{\left(1,010\frac{\Delta C}{\sqrt{3}}\right)^2 + \left(0,005\frac{\Delta V}{\sqrt{3}}\right)^2 + \left(0,0001\frac{\Delta S}{\sqrt{3}}\right)^2 + \left(1,320\frac{\Delta P}{\sqrt{3}}\right)^2 + \left(0,092\frac{\Delta T}{\sqrt{3}}\right)^2} \quad , \quad (3)$$

where ΔC − content of basic component, mg/cm^3;
ΔV − packing options (volume of ampoule), cm^3; ΔS − solvent options;
ΔP − manufacturer of medicinal product; ΔT − ambient temperature.

If the bias is insignificant, the correctness of the method is calculated from formula

$$\Delta_{c,m} = 1,96\sqrt{\frac{S_m^2}{L} + \frac{\Delta_{0m}^2}{3} + \sum_{\xi=1}^{P}\left(\frac{\partial C_i}{\partial \Delta П_\xi}\right)^2 \cdot \Delta^2(\Delta П_\xi)} = 1,96 \cdot \sigma_{c,m} \quad , (4)$$

where S_m^2 − dispersion, characterizing the spread of the measurement results under reproducibility conditions, mg/cm^3;
L − number of measurement results, cm^3;
Δ_{0m}^2 − error of measurement result obtained with the help of GVET 176-1-2010, mg/cm^3.

The obtained accuracy indicators are presented in Table 1.

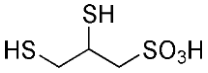
Table 1 Range of measurements, values of accuracy, repeatability and reproducibility

Measuring range, measured value	Repeatability, σ_r	Reproducibility, σ_R	Accuracy, ±δ
from 0 to 1,0 correlation coefficient	0,008 abs.	0,013 abs.	-
от 1 до 350 mg/cm^3, mass concentration	5 rel. %	8 rel. %	20 rel. %

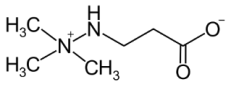
In 2018 FGUP “UNIIM” carried out special proficiency testing for Roszdravnadzor laboratories in the field of quantitative determination the content of the basic components by the Raman spectroscopy method, round: MSI 241-L2 (RS) -1/2018 and in the field of authenticating (authenticating) means, round: MSI 241-Л1 (RS) -1/2018.

The following medicines have been chosen as test samples:

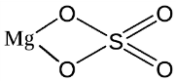
Unithiol-ferein
(2,3-Sodium dimercaptopropanesulfonate)



Meldoney
(2 (2-Carboxylatoethyl) -1,1,1-trimethylhydrazinium)



Magnesium sulfate



Traceability of measurement results during proficiency testing conducting provides with the help GVET 176-1-2010. The traceability scheme is shown in Figure 1.

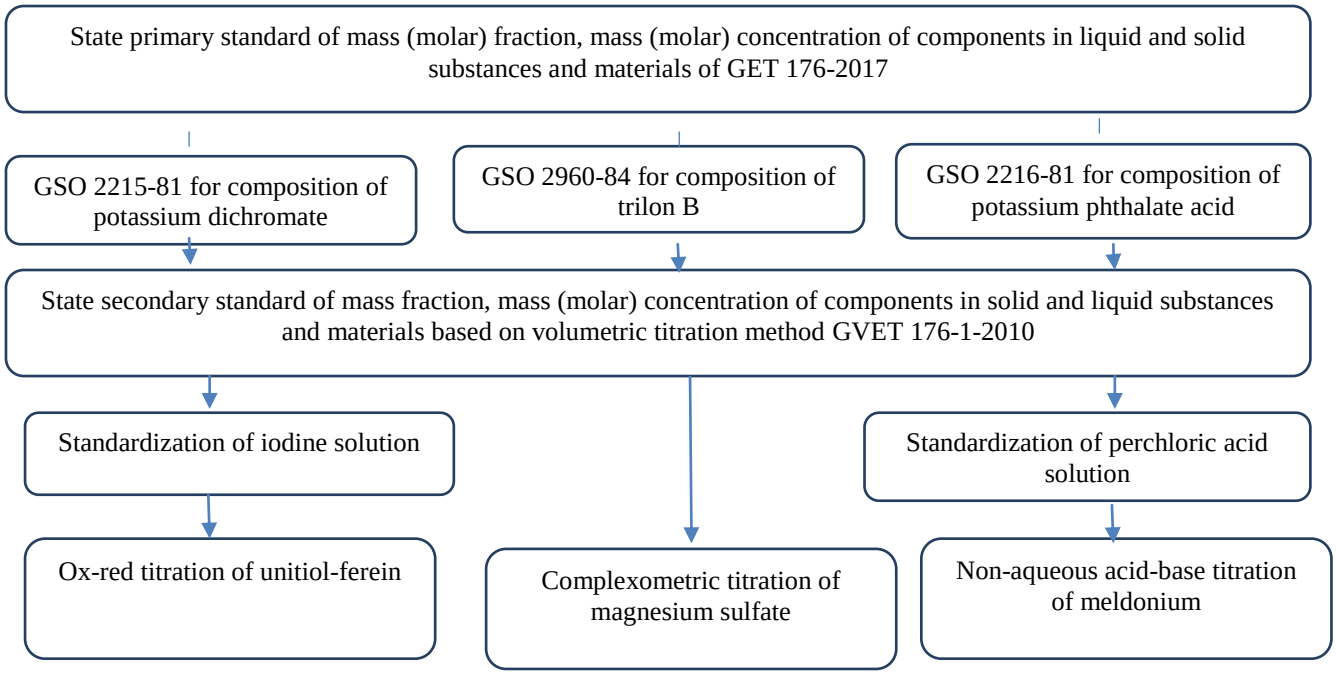


Fig. 1. Scheme of metrological traceability using GVET 176-1-2010

The quality of the measurement results has been evaluated in accordance with ISO/IEC 17043 [7] and ISO 13528 [8] by comparing the values of z indices with the established control standards.

All participants of proficiency testing during the implementation of the measurement procedure based on Raman spectroscopy in the field of authentication (identification) and in determining the indicator “content of the main component” in injecting drugs showed satisfactory results.

Thus, the metrological characteristics of the identification technique and the subsequent quantitative determination of the content of the basic components by the Raman method for drugs in an injection form are confirmed.

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ON THE DEVELOPMENT OF A CERTIFIED REFERENCE MATERIAL OF GLUTEN

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Keywords: gluten, certified reference material, ELISA method, food safety, celiac disease

In accordance with the Codex Alimentarius Commission document [1], gluten is defined as the protein fraction of wheat, rye, barley, oats or their hybrids and derivatives from this protein fraction that may be intolerable by some people. Gluten consists of prolamines and glutelins. The content of gluten directly depends on the content of prolamine.

Gluten content control in food products plays a key role in ensuring the safety of food intended for patients with celiac disease that is a chronic, progressive, hereditary disease characterized by persistent gluten intolerance to cereals with the development of atrophy of the small intestinal mucosa and associated malabsorption syndrome. According to international organizations, up to 1% of the world's population suffers from this disease [2]. The only way to treat celiac disease and prevent its complications is a strict and life-long gluten-free diet. Requirements for the content of gluten in certain types of specialized food products are established in the international documents of Codex Standard 118 [1] and ALINORM 08/31/26 [3], prepared by the Codex Alimentarius Commission of Nutrition and Food for special diets (CCNFSD). There is Technical Regulations "On the safety of certain types of specialized food products, including dietary curative and dietary preventive nutrition" [4] in the territory of the Customs Union.

According to the international document [4,5], ELISA is the recommended method for determination of gluten content in food ingredients and prepared foods. The choice in favor of the ELISA method was made in view of its specificity, sensitivity and suitability for routine analysis.

The ELISA method is based on an enzyme-linked immunoassay, in which the labeled antibodies to gliadin form a chemically strong complex that changes the color of the products of chemical reactions, followed by measurement of the absorbency. ELISA method is implemented in test systems produced by various manufacturers and based on the use of antibodies that were induced to various prolamine fractions or specific sequences that are toxic. Different test systems don't always give the same results for the determination of gluten content in the same food or food ingredients, as demonstrated, for example, in [6-8] and also in Figure 1.

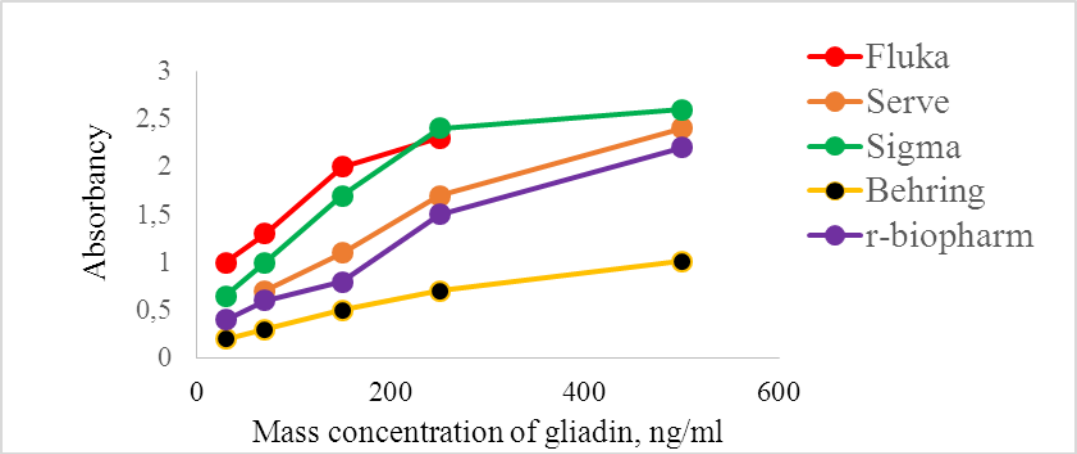

Fig.1. Effect of the use of various reference materials for calibration of test systems

Up to date, the best-characterized reference material is the reference material of gliadin (further – PWG-gliadin) developed by the Working Group on Prolamins and Toxicity (PWGAT). The extraction procedure and characterization of gliadin CRM is described in detail in [9]. PWG gliadin is a gliadin powder obtained by extracting gliadin from flour made from 28 of the most common European wheat varieties.

The Institute for Reference Materials and Measurements (IRMM, Belgium) initially approved the PWG-gliadin as a certified reference material, but soon withdrew this decision. In practice, it turned out that the creation of CRM that contains from 28 different varieties of wheat led to difficulties in measurements, to the high cost of CRM, and did not lead to a decreasing in the spread during measurements with the help of different test systems.

Thus, despite the large number of works devoted to this issue, to many manufacturers of test systems, the question of metrological assurance remains unresolved.

FGUP “UNIIM” together with the company “Xema” and the Institute of Physical Chemistry and Electrochemistry, Moscow has begun work for creation of CRM of gliadin. The starting material was wheat of solid flour. For gliadin getting the wheat flour was used. Gliadin was extracted from this flour with the help of 70% ethyl alcohol. Qualitative and quantitative analysis was carried out at the Institute of Physical Chemistry and Electrochemistry. This analysis was conducted on a liquid chromatograph with mass-selective detector under reversed phase chromatography conditions with gradient elution. The results are shown in Table 1.

The results presented in Table 1 were used to calculate the nitrogen-to-protein conversion factor.

Mass fraction of nitrogen in the sample of gliadin was determined with the help of 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). The validity of GVET 176-1-2016 usage is explained by the results of successful key comparisons CCQM-K130 “Mass fraction of nitrogen in glycine”.

T a b l e 1 Aminoacids content in the gliadin hydrolyzate obtained by HPLC/MS

Aminoacids	Glycine	Alanine	Valine	Leucine	Serin	Glutamic acid	Glutamine	Aspartic acid	Asparagine	Phenylalanine
C, mg/cm^3	<0,01	<0,01	1,2	124,4	0,16	9,3	-	-	5,4	4,2
%, (mass)	<0.003	<0.003	0.446	37.015	0.048	2.767	-	-	1.607	1.205
Aminoacids	Lysine	Arginine	Histidine	Cysteine	Tryptophan	Proline	Methionine	Treoini	The total content	
C, mg/cm^3	-	0,06	0,06	-	-	20,6	<0.01	145.9	336,08	
%, (mass)	-	0,018	0,018	-	-	6,129	<0.003	43.412	100	

Characterized solution of gliadin in 70% alcohol was used to build a calibration curve for the test systems produced by the company “HEMA”. This test system uses the principle of a two-site (sandwich) enzyme immunoassay.

Conclusions

1. Gliadin was obtained from wheat flour by repeated extraction with 70% alcohol.

2. The Aminoacids composition of the gliadin solution was determined by the HPLC/MS method. The results of this experiments allowed to estimate the nitrogen-to-protein conversion factor.

3. Nitrogen mass fraction in the gliadin alcohol solution was determined with the help of GVET 176-1-2010 having confirmed calibration and measurement capabilities in the international BIPM database, that ensures the traceability of measurements of the mass fraction of nitrogen (gliadin protein) to SI units.

4. The prepared candidate material to CRM was tested for calibration of the test system produced by the company “HEMA”. Preliminary accuracy characteristics for this test system are obtained.

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COMAR, WHERE DO YOU GO?

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In the late 1970s, COMAR was setup to shed light on the availability of RMs worldwide. For a long time, it was a reputed international directory, and the only one that helped finding those rare, high-quality CRMs.

But the scene has changed dramatically in the meantime. Today, major resellers maintain databases with 100,000s of RMs or CRMs, and the market has become big business dominated by large international players.

So, the question arises whether there is a future for COMAR. At BAM we believe there is, and are working on it. We would like to present our current efforts and invite you to share your thoughts with us.

ISOTOPE DILUTION MASS SPECTROMETRY IN THE DEVELOPMENT OF REFERENCE MATERIALS

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Isotope dilution mass spectrometry is recognized by Consultative Committee for Amount of Substance (CCQM) as a method, which may be considered a primary measurement method. The method of isotope dilution mass spectrometry (IDMS) has a number of advantages over other analytical methods.

The priority task in the development of the isotope dilution method in inductively coupled plasma mass spectrometry is the development and creation of the range of reference materials of isotope-enriched composition of elements. Since 2012, Ural Research Institute for Metrology (UNIIM) has been studying the possibility of applying the IDMS for creating reference materials for composition and properties of substances and materials. UNIIM has at the same time been engaged in the development of isotope-enriched reference materials of approved type. Studies are carried out using an Inductively Coupled Plasma Mass Spectrometer NexION 300D (“Perkin Elmer”), included in National Secondary Standard for the Units of Mass Fraction and Mass (molar) Concentration of Metals in Liquid and Solid Substances and Materials GVET 196-1-2012.

To date the following certified reference materials have been developed:

- certified reference material for isotopic composition of nickel, enriched by ^{60}Ni isotope , in nitrate solution (^{60}Ni CRM UNIIM) – GSO 10273-2013;
- certified reference material for isotopic composition of lead, enriched by ^{206}Pb isotope, in nitrate solution (^{206}Pb CRM UNIIM) – GSO 10274-2013;
- certified reference material for isotopic composition of cadmium, enriched by ^{111}Cd isotope, in solution (^{111}Cd CRM UNIIM) – GSO 10493-2014;
- certified reference material for isotopic composition of silver, enriched by ^{107}Ag isotope, in solution (^{107}Ag CRM UNIIM) – GSO 10494-2014.

Taking into account a substantial demand for such CRMs, materials have been prepared for the further development of isotope-enriched CRMs for isotopic composition of chrome, thallium, magnesium, strontium, rubidium, copper, zinc, etc.

While developing the above-mentioned CRMs, UNIIM is also engaged in tests and implementation of the IDMS method using developed CRMs when conducting a variety of measurements relating to the scientific work, as well as when conducting tests with the purpose of type approval.

The IDMS method was successfully implemented using the above-noted certified reference materials when developing reference materials for composition of various matrices, such as pure metals and alloys, some food products. Method application is tested on matrix analysis, having problematic “incomplete determination” of the element as a result of incomplete chemical decomposition. This may be incomplete dissolution, for example, of complex geological objects, partial volatilization of an element or coprecipitation in case of matrix removal. The use of the IDMS makes it possible to obtain well-reproducible and comparable values of mass fractions of impurity elements, including in complex matrices, which provides more accurate measurement results. It is important to note that in some cases the use of the IDMS method makes it possible to decrease the time of sample preparation.

Based on the studies conducted, it has become possible to improve the measurement standard in terms of isotopic ratio measurements and application of the IDMS method.

TECHNIQUES FOR AMBIENT AIR MONITORING. CERTIFICATION AND ORGANIZATION OF THE INTRALABORATORY QUALITY CONTROL OF MEASUREMENTS CONDUCTED USING REFERENCE MATERIALS

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Keywords: ambient air analysis techniques, workplace air, atmospheric air, emissions, certification, operational control, stability control, analytical stage, sampling

In this work, an experimental and computational approach is proposed for the certification and organization of an intra-laboratory quality control of various techniques used for monitoring ambient air, including workplace air, atmospheric air and industrial exhaust gases using standard gas reference materials.

It is a common knowledge that such air environments as workplace air, ambient air and industrial exhaust gases are characterized by a high variability, instability and heterogeneity against standard environmental indicators. Therefore, it is frequently impossible to collect two or more duplicate samples, as well as to store the collected samples for a long time. Due to these reasons, the certification of air monitoring techniques, for which reference gas mixtures and micro-stream sources are not provided, can be a challenging task. Thus, it is known that most techniques for monitoring workplace air and ambient air [1] are not certified; therefore, they cannot be applied in the sphere of state regulation for ensuring the uniformity of measurements.

The RF sanitary-hygienic standard 2.2.5.3532-18 [2] establishes maximum permissible concentrations for impurities in workplace air for over 2,500 substances. In addition, the RF sanitary-hygienic standard 2.2.5.2308-07 [3] gives approximate permissible concentrations for another 580 substances. Therefore, only workplace air monitoring requires about 3,000 certified techniques.

It should be noted that there is a small number of standard gas reference materials for monitoring air impurity levels – control gas mixtures (CGMs), for less than thirty substances with established maximum permissible concentrations. These substances are inorganic gases and light organic compounds. In addition, about a hundred of gas analysis instruments (micro-stream sources), including for monitoring light organic compound impurities, have been developed. The existing number of gas reference materials hinders the development of indicators (on the basis of a certification experiment) that would allow the accuracy of an applied air quality monitoring technique to be estimated. As a result, it is impossible to establish quality standards for the intra-laboratory control of the majority of air monitoring techniques and to implement the procedures of operational and stability control.

The proposed approach is based on the division of an applied monitoring technique into two stages: sampling and the analysis of the collected sample. For the sampling stage, the computational and experimental method of uncertainly value determination is applied. For the analytical stage, an experimental method is used, similar to other condensed medium analysis techniques.

The described approach can be used for assessing air monitoring techniques, which procedures involve sampling using a liquid or solid absorber of impurities under monitoring (such as solid adsorbents, filters, liquid absorbers), with the impurities being condensed and consequently analysed. The division of monitoring techniques into the aforementioned stages (sampling and analysis) is conditional. The proposed approach cannot be applied to techniques that use indicator tubes and automatic gas analysers.

Within the framework of the proposed approach, indicators for assessing the efficiency of air monitoring techniques, as well as the measurement uncertainty values, are established separately for each of the aforementioned stages. The value of the sampling stage accuracy (δ_{on}) is calculated using a computational and experimental method. Using the passport specification data of a measurement instrument used for sampling, the values of measurement uncertainly can be calculated, as well as the rate of air aspiration through the absorber, time of air aspiration, air temperature and pressure during sampling. The measurement uncertainly in the analytical stage is determined taking into account the uncertainly value of sample preparation and that of obtaining measurement information on the analytical sample composition. The measurement uncertainty characteristics of the analytical stage (including the analytical stage accuracy, δ_a) are estimated experimentally using algorithms given in the Interstate Standardization Recommendations (ISR) 61-2010 [4].

The experimental evaluation of the analytical stage uncertainly can be performed using clean absorbers in a number sufficient for reliable assessment. These absorbers should contain the identical amount of the reference material or certified gas mixture of an impurity under determination. In this case, as many duplicate measurements as necessary can be carried out (to provide intra-laboratory precision).

During the primary certification of an air monitoring technique, inter-laboratory experiments are used to determine the following indicators of the analytical stage uncertainty:

- repeatability of the analytical stage ($\sigma_{r,a}$);
- reproducibility of the analytical stage ($\sigma_{R,a}$);
- correctness of the analytical stage ($\delta_{c,a}$);
- accuracy of the analytical stage (δ_a).

The obtained values of the monitoring technique accuracy are compared with those specified in the state normative documents.

The accuracy indicator of a technique (δ) is estimated by summing δ_{op} and δ_a according to the formula:

$$\delta = \sqrt{\delta_{on}^2 + \delta_a^2} \quad , (1)$$

When implementing the technique under certification in a laboratory, the intra-laboratory control of the quality of the quantitative chemical analysis is carried out according to RMG 76-2014 [5] and GOST R ISO 5725-2002 [6]. In this case, the quality of measurement results obtained at the analytical stage of the technique is controlled. For this, controlling instruments similar to those used when assessing the indicators of measurement uncertainly values in the analytical stage are applied. For example, for measurement techniques based on air aspiration through a filter, filters are produced with the identical amount of the substance under investigation (a portion of the reference material with the certified content). For a technique based on air aspiration through a liquid absorbent, in which the impurity under investigation is dissolved or chemically reacted with the liquid absorber, liquid absorbers are prepared with the inserted identical amount of the reference material or certified mixtures of the impurity under study.

This paper demonstrates how the intra-laboratory control of the analytical stage can be organized. The algorithms of operational and stability control, including Shewhart control charts, are presented. The proposed approach facilitates the certification of air monitoring techniques for use in the field of state regulation for ensuring the uniformity of measurements.

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REFERENCE MATERIALS OF CATALYTIC ACTIVITY AS A MEANS OF PROVIDING THE METROLOGICAL TRACEABILITY OF MEASUREMENT RESULTS. KATAL

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Keywords: metrological traceability, state primary standard katal, catalytic activity, catalytic concentration, laboratory medicine, heterogeneous solid catalysts, hierarchy of calibrations

Every person wants to be healthy, live a long and happy full life, exciting life. In truth, there are people who challenge this position. But still we will adhere to the point of view that for every person it is important to have reliable information about the condition of his body, including the results of tests, diagnosis and the appointment of adequate treatment. It is clear that for this there must be a strong healthcare system, which we have created, but also the existence and full operation of the metrological system in laboratory medicine, ensuring metrological traceability of measurement results, is absolutely necessary.

In accordance with the Federal Law No. 102-FZ of 26.06.2008 “On ensuring the uniformity of measurements” [1], the concept of traceability is a property of a measurement standard, a measuring instrument or a measurement result, consisting in a documented establishment of their connection with a state primary measurement standard or the national primary measurement standard of the foreign state of the corresponding unit of magnitude by comparing the standards of units of quantities, verification, calibration of measuring instruments.

Metrological traceability [2] is a property of a measurement result, according to which the result can be correlated with the basis for comparison through a documented continuous chain of calibrations, each of which contributes to measurement uncertainty.

We see our role in providing conditions for improving the quality of the results of analyzes, comprehensive metrological support for clinical diagnostic laboratories, chemical-toxicological laboratories and laboratories that carry out measurements of human body parameters.

The set goal is achieved through the development of the State primary measurement standard of catalytic activity unit - katal, the participation in international comparisons, development of standard samples of analyzed substances in serum, blood plasma, development and certification of measurement techniques and reference measurement techniques, creation of digital metrology for laboratory medicine.

The metrological characteristics of the experimental sample of the State primary measurement standard of a unit of catalytic activity of biological and chemical substances - Katal are given in Table 1 [3].

T a b l e 1. Metrological characteristics of the measurement standard Katal

Name of metrological and technical characteristics	Value of metrological and technical characteristics
Range of measurements of catalytic activity (catalytic concentration) of biological substances, kat/dm^3	from $7{,}8\cdot10^{-7}$ to $9{,}4\cdot10^{-6}$
Range of measurements of catalytic activity (specific catalytic activity) of chemical substances, kat/g	from $1\cdot10^{-8}$ to $2\cdot10^{-7}$
Extended uncertainty of the measurement of catalytic activity (k=2), %	from 0,5 to 4

The issue of developing standard samples that must be consistent with measuring tasks, to be commutative to the analyte to ensure the measurement of catalytic activity, is quite acute.

Manufacturers and developers of modern methods and diagnostic tools are faced the need for metrological support for their development in testing, calibration and calibration of new measuring instruments, approbation of developed techniques.

For such measuring instruments, traceability is expediently provided with the help of solutions with known catalytic activity (catalytic concentration), known concentration of target analytes approved as GSO.

Foreign manufacturers produce calibration mixtures for factory testing of their analyzers, which can potentially be used for metrological support of modern devices, but they are expensive, and their composition is a trade secret, which makes it difficult to approve them as reference materials.

Our laboratory of metrological support of biological and information technologies, from our side, makes a feasible contribution to the solution of this problem. For example together with FGBU ”FNIISEM im. N.F. Gamaleia” of the Russian Ministry of Health in 2017, three standard samples were approved - the mass concentration of the recombinant protective antigen Bacillus anthracis in phosphate-saline solution, the mass concentration of the recombinant protein GP of the Ebola virus and the mass concentration of the recombinant toxin Clostridium Difficile [4], which have the metrological characteristics given in Table 2.

T a b l e 2. Metrological characteristics of standard bioassay samples tested by our laboratory in 2017.

Name of the certified characteristics	Interval of allowed certified values, ng/ml	Limits of permissible values of the relative measurement error δ, at P = 0,95,%
The mass concentration of the recombinant protective antigen Bacillus anthracis	from 20 to 30	± 22
The mass concentration of the recombinant protein GP of the Ebola virus	from 20 to 30	± 22
The mass concentration of the recombinant toxin Clostridium Difficile	(from 500 to 1000) ng/μL	± 7

In the current year, our laboratory develops and tests standard samples of the catalytic concentration of enzymes with a certain catalytic activity, designed for calibration and verification of bioanalytical measurement instruments.

The measurement standard Katal also includes standard samples of solid-state heterogeneous catalysts, which are used, including for the implementation of exhaust gas purification processes.

In 2011, the Government of the Russian Federation made rational use of natural resources one of the priority areas for the development of science and technology. The constant increase in the volume of production and consumption of fuel and the number of vehicles leads to an increase in the volume of harmful substances entering the atmosphere, such as hydrocarbons, hydrogen sulphide, sulfur oxide, carbon monoxide, nitrogen oxide, various types of solid particles. The quality of exhaust gas purification directly affects the amount of harmful substances emitted to the atmosphere.

The quality of solid catalysts is primarily determined by their activity, which in turn depends on a complex of different parameters, such as the concentration of components, the surface area, the size of the catalyst pellets ets.

In 2018, we plan to test the standard samples of the aluminum-magnesium chromium catalyst IK-12-72 and the oxide aluminomanganese catalyst, IKT-12-40, developed by the Institute of Catalysis named after. G.K. Boreskov SB RAS. Catalytic activity will be expressed in units of catalytic activity - in katal, referred to as grams of catalyst.

Aluminum magnesium chromium catalyst IK-12-72 is a ball of dark green color with a diameter of 1.0-1.6 mm. The composition of the catalyst includes Cr_2O_3, MgO, the rest is Al_2O_3. The range of catalytic activity (specific catalytic activity) of the aluminum-magnesium chromium catalyst IK-12-72: from 8.8 · 10-8 to $9.5 \cdot 10^{-8}$ kat/g. Absolute error in measurements of catalytic activity (k = 2): $1.5 \cdot 10^{-8}$ kat/g.

The alumo-manganese oxide catalyst IKT-12-40 is cylinders with a diameter of 3 mm and a length of 3-5 mm. The catalyst composition includes Mn_2O_3 and Al_2O_3. The range of catalytic activity (specific catalytic activity) of the oxide-based aluminum-manganese catalyst IKT-12-40: from $3.8 \cdot 10^{-8}$ to $5.3 \cdot 10^{-8}$ kat/g. Absolute error in the measurement of catalytic activity (k = 2): $0.7 \cdot 10^{-8}$ kat/g.

The result of the work of creating standard samples ensuring accurate results of measurements of catalytic activity will be the construction of calibration hierarchies for demanded facilities established on the basis of the List of Critical Technologies of the Russian Federation, state programs “Development of the pharmaceutical and medical industry for 2013-2020”, “Industry Development and increasing its competitiveness for the period until 2020”.

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CONFORMITY ASSESSMENT OF MULTICOMPONENT MATERIALS – WHO AND WHY TAKES RISKS?

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Keywords: conformity assessment; multicomponent materials; measurement uncertainty; correlated test results; risks of false decisions

Standard specifications for the chemical composition of a multicomponent material – a denatured alcohol, medication, an environmental compartment, alloy, etc. - limit the actual ('true') concentration ci of the *i*-th component, $i = 1, 2, \ldots, n$, including base components, impurities or groups of impurities. Conformity assessment of a material batch is based on comparing the concentration test/measurement results cim with such specification limits. Since any cim value has an associated measurement uncertainty [1], several kinds of risk of a false decision on conformity of a batch may be defined. The probability of accepting a batch of the material when it should have been rejected is named 'consumer's risk', whereas the probability of falsely rejecting the batch is the 'producer's risk'. For a specified batch, they are referred to as the 'specific consumer's risk' and the 'specific producer's risk' R^*_{ci} for the i-th particular component of the material under control. The risks of incorrect conformity assessment of a batch randomly drawn from a statistical population of such batches are the 'global consumer's risk' and the 'global producer's risk' R_{ci}, as they characterize the material production globally [2].

In general a component-by-component evaluation of the risks of a material conformity assessment is not complete, as this approach does not give an answer to the question of the probability of a false decision on conformity of the material as a whole. When conformity assessment for each *i*-th component of a material is successful (i.e. the particular specific R^*_{ci} or global R_{ci} risks are small enough), the total probability of a false decision concerning the material as a whole (the total specific R^*_{total} or total global R_{total} risk) might still be significant [3]. Using the law of total probability relating marginal probabilities to conditional probabilities, the total risk can be evaluated as a combination of the particular risks whenever the variables (actual component content values ci, and corresponding test results c_{im}) are independent. When the number *n* of components of the same material under control increases, the total risk also increases [4, 5].

Evaluating total risk for correlated quantities has been discussed in our paper [6], where specification limits of the active components' contents in tablets of a multicomponent medication were interpreted as a multivariate specification domain. Actual values of components' contents and corresponding test results were modelled by multivariate distributions, and the total global risk of a false decision on the material conformity was evaluated based on calculation of integrals of their joint probability density function. A total specific risk was evaluated as the joint posterior cumulative function of actual values of a specific batch lying outside the multivariate specification domain, when the vector of test results, obtained for the batch, is completely inside this domain. It was shown that the influence of correlation on the risk is not easily predictable.

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DEVELOPMENT OF CERTIFIED REFERENCE MATERIALS FOR MASS FRACTION OF ELEMENTS IN SOLID MATRIX FOR METROLOGICAL ASSURANCE OF X-RAY FLUORESCENCE AND ATOMIC EMISSION ANALYSIS

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Keywords: reference material, X-ray fluorescence analysis, atomic emission analysis, sodium mass fraction, chlorine mass fraction, lead mass fraction, iron mass fraction, solid matrix

At present, certified reference materials (CRMs) of the mass fraction of elements in a solid base are produced in the Russian Federation, the metrological characteristics of which are established by the calculation-experimental method. In carrying out such a procedure, two or more precursor components are mixed with a known composition and then the mixture is compressed. The loss of components during the homogenization of the mixture is not taken into account. The disadvantage of this method is the lack of control of the certified value of CRM after mixing the starting materials.

The purpose of this work was to develop a CRM for mass fraction of sodium and chlorine in a solid matrix, CRM for mass fraction of iron in a solid matrix, CRM for mass fraction of lead in a solid matrix, the metrological characteristics of which are established using the State primary standard of the mass (molar) fraction and mass (molar) concentration of the components in liquid and solid substances and materials based on coulometry GET 176-2017, the composition and metrological characteristics of which were described earlier [1, 2]. The main purpose of these CRMs is verification, calibration and tests of X-ray fluorescence and atomic emission spectrometers, including tests for type approval.

The material of CRM for mass fraction of sodium and chlorine in the solid matrix is a sodium chloride, pressed in the form of disks with a diameter of (30 ± 1) mm, height of (4.5 ± 0.5) mm.

The material of CRM for mass fraction of lead in the solid matrix is a mixture of lead (II) nitric acid and boric acid, pressed in the form of disks with a diameter of (30 ± 1) mm, height of (4.5 ± 0.5) mm.

The material of CRM for mass fraction of iron in the solid matrix is a mixture of iron (III) oxide and boric acid, pressed in the form of disks with a diameter of (30 ± 1) mm, height of (4,5 ± 0,5) mm.

The method of preparing samples in the form of the pressed tablets without binding additives and with binder additives is widely used and described in [3].

Metrological characteristics of CRMs were established using the State primary standard GET 176-2017: for the CRM of sodium and chlorine in the solid matrix the method of coulometric titration was applied, for the CRMs of lead and iron in the solid matrix the method of controlled-potential coulometry was used.

Standard uncertainty from material heterogeneity of CRMs was determined in accordance with [4].

The stability of the material was confirmed by measuring the mass fraction of the elements for three years at regular intervals on the CRMs material manufactured earlier. Estimation of relative standard uncertainty from instability was carried out in accordance with [4].

The metrological characteristics of CRMs are presented in Tables from 1 to 3.

T a b l e 1. Metrological characteristics of CRM for mass fraction of sodium and chlorine in a solid matrix

(NaCl-SM CRM UNIIM)

Certified characteristic of CRM	Certified value, %	Relative expanded uncertainty of the certified value, U, % (k=2)	Limits of the relative error of the certified value, δ, % (P=0,95)
Mass fraction of sodium	39,3	0,1	±0,1
Mass fraction of chlorine	60,7	0,1	±0,1

T a b l e 2. Metrological characteristics of CRM for mass fraction of lead in a solid matrix (Pb-SM CRM UNIIM)

Certified characteristic of CRM	Certified value, %	Relative expanded uncertainty of the certified value, U, % (k=2)	Limits of the relative error of the ertified value, δ, % (P=0,95)
Mass fraction of lead	1,03	3	±3

T a b l e 3. Metrological characteristics of CRM for mass fraction of iron in a solid matrix (Fe-SM CRM UNIIM)

Certified characteristic of CRM	Certified value, %	Relative expanded uncertainty of the certified value, U, % (k=2)	Limits of the relative error of the certified value, δ, % (P=0,95)
Mass fraction of iron	0,96	3	±3

The developed CRMs are included into the State Register of Approved Reference Material Types. The information is presented in Table 4.

T a b l e 4. Information on the introduction of developed CRMs into the State Register of Approved Reference Material Types

Number of CRM in the State register of type approved RMs	Name of CRM
10934-2017	CRM for mass fraction of sodium and chlorine in a solid matrix (NaCl-SM CRM UNIIM)
10991-2017	CRM for mass fraction of lead in a solid matrix (Pb-SM CRM UNIIM)
11036-2018	CRM for mass fraction of iron in a solid matrix (Fe-SM CRM UNIIM)

Traceability of the certified values of CRMs is ensured by using the method of direct measurements at the 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 CET coulometry 176-2017.

In 2018, Ural Scientific Research Institute for Metrology plans to develop and produce a CRM for the mass fraction of boric acid in a solid matrix to be used as a background sample in X-ray fluorescence and atomic emission analysis. In the future, it is planned to expand the nomenclature of CRMs for the mass fraction of elements in a solid matrix.

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REFERENCE MATERIAL PRODUCER - VIMS: KEY ASPECTS OF ENSURING THE QUALITY OF CERTIFIED REFERENCE MATERIALS OF SOLID MINERAL RESOURSES

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FSBI “VIMS” has all the necessary resources to perform a full range of works on the production of CRMs, 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. The institute carries out the works on the production of CRMs (including multi-element) of various types of mineral raw materials and products of their processing: polymetallic ores, ferrous and non-ferrous metals ore, rare earth metals, etc. FSBI “VIMS” is accredited in the field of production of CRMs in the international organization for the accreditation of laboratories ILAC (International Laboratory Accreditation Cooperation) - APLAC (Asia Pacific Laboratory Accreditation Cooperation) for compliance with the requirements of the International Standard ISO Guide 34:2009 “General requirements for the competence of reference material producers” (Guidance of ISO 34:2009 “General requirements for the competence of producers of reference materials”). The accreditation confirms technical competence of the producer of CRMs in the declared area of accreditation and the functioning of its quality management system.

One of the main aspects of ensuring the quality of CRMs of solid minerals is the process approach to work organization. To ensure the quality of each stage of production of CRMs, control procedures have been developed and implemented.

High quality of the performed works and constant increase of their effectiveness and economic efficiency is achieved through introduction and application of international approaches to the management system, the use of only reliable (proven) modern production equipment and advanced information technologies.

ANALYSIS OF THE INDUSTRY BASE OF CERTIFIED REFERENCE MATERIALS OF MINERAL RAW MATERIALS

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On behalf of the Federal Agency for Subsoil Use (Rosnedra), the FSBI “VIMS” has developed and maintains the Industrial Register of Certified Reference Materials approved (recommended) for use in laboratory analytical support for geological exploration for solid minerals (hereinafter Industry Register of CRMs). The main purpose of updating the registry is to provide reliable information to laboratories performing analytical work in the field of subsoil use. Up-to-date information is available at FSBI “VIMS” website (vims-geo.ru). As of the second quarter of 2018 the Industry Register of CRMs contains more than 900 items of CRMs of the various categories.

State CRMs (GSO) are mainly represented in the Industry Register by subsurface rocks and alloys based on precious metals for which the shelf life is 20 years or more. Due to low consumption of the material of rock composition State CRMs, as well as the availability of sufficient material, the developers of these State CRM types extend their shelf life, unlike to the material of reference material of the branches (BRM) and in-house reference material (IHRM). A significant part (about 70%) of the nomenclature of reference materials of the BRM category is represented by ores of precious metals, as well as by the products of their processing. This is also due to the fact that enterprises engaged in geological exploration for solid minerals (exploration, production) tend to have reference materials (often sets of reference materials) corresponding to the matrix ores of the developed deposit to ensure reliable results of analytical studies. However, despite a significant number of these types of reference materials, as well as a fairly large production lot (about 100-200 and more kilograms), analytical weighments for the determination of precious metals reach 50 g which in turn leads to a rapid consumption of the entire batch of reference materials. By the end of shelf life (typically 5 years), and often much earlier, the material is already physically exhausted, which eliminates the need for extension.

A significant increase (by 46 % in 2017) in number of in-house reference materials is connected with the fact that customers (usually they are mining plants and gold extracting factories extracting and processing precious metal ores) develop in-house reference material thereby reducing the cost of certification and approval of CRMs.

As an additional information, the Industry Register contains information on CRMs with expired validity period (Section V: “CRMs with expired certificate validity, and CRMs which are excluded from registers. Information data”).

PRODUCTION AND CERTIFICATION OF REFERENCE MATERIALS OF BORON MASS FRACTION IN SILUMIN

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Keywords: reference materials of silumin, certified boron content, production, evaluation of characteristics

At the AIC - the Russian Arbitration Laboratory for Nuclear Materials Testing (AIC-RAL) of the UrFU the work on the production and testing of reference materials (RMs) of the mass fraction of boron in silumin (the SOBor set) has been completed. The customer was PJSC “Machinostoitelny zavod” (MSZ Electrostal). A set of four materials is intended for calibrating the equipment for atomic emission analysis of silumin and corundum, attestation and control of the accuracy of the methods for measuring the composition of silumin.

Aluminum alloys are the main structural materials in aircraft construction, shipbuilding, nuclear industry. In the nuclear industry, boron is one of the critical impurity, which is associated with its high ability to absorb thermal neutrons. Therefore, the content of boron in the applied aluminum alloys, in particular silumin, is normalized at a sufficiently low level (mass fraction - not more than 3.10^{-3} %). Determination of the mass fraction of boron from 1.10^{-4} % is carried out by a highly sensitive atomic emission method with arc excitation of the spectrum after preliminary transfer of the object into the oxide form.

In the preparation of RMs, a technology has been implemented that made it possible to establish the metrological characteristics of the materials according to the calculation and experimental procedure in accordance with MI 1992-98. The choice and preparation of the RM matrix was a certain complexity. The best option providing the required concentration of the certified element and the adequacy of the oxidized silumin to its chemical form was an artificial mixture of elemental silicon with aluminum and nickel oxides. A material with a maximum boron content (SOBor-1) was obtained by introducing a solution of sodium tetraborate into the matrix, followed by heat treatment, grinding and homogenization. The next two materials of the set were synthesized by successive dilution of the SOBor-1 by matrix with the homogenization of the materials in the mixer. The matrix material was used as the sample with the minimum concentration of the attested element (SOBor-4). Such a method of preparation of a kit, based entirely on metrologically sound synthesis procedures, makes it possible to carry out the certification of materials using the calculation method, taking into account data on the degree of heterogeneity of the materials.

The tests of the RM of the set included estimation of the homogeneity of the boron distribution, determination of its content at the matrix, evaluation of the mutual consistency of the materials in the set and the stability of the composition. To establish homogeneity 10 samples of each material were taken uniformly along the mixer's height during unloading. The boron was determined in a leaching solution by a mass spectral method on an Elan 9000 spectrometer. Portions of materials to form an analytical signal was 10 or 30 mg. The relative standard deviations of the chemical inhomogeneity of the boron distribution in the RM set at the representative sample (0.1 g) were from 0.6 to 1.71 % and were taken into account in calculating the error of RM.

The content of the certified element in the matrix material was determined by the method of additives according to the certified method in the laboratories of AIC-RAL and “MSZ”. During the implementation of the method, for the metrological provision of which the released set is intended,

the mutual consistency of the materials in the set was established. Metrological traceability of the certified values of RM to mass units is realized using the verified scales and the certified atomic-emission method for measuring the mass fraction of boron in silumin, intermetallide, electrocorundum. The mass fraction of boron was calculated relative to the sum of the masses of aluminum, silicon and nickel in silumin and ranges from 1.10^{-4} to $3.3.10^{-3}$ % with a relative error not exceeding 4 %. The shelf life of the specimen, estimated by the method of accelerated aging under conditions of increased thermal and vibration loads, is set at 60 years.

TECHNIQUE OF CONTROLLING THE CONTENT OF Ce AND Gd IN YGAG:Ce POWDERS BY MEANS OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Keywords: phosphors, inductively coupled plasma mass spectrometry, yttrium-aluminum garnet, cerium, gadolinium, powder, fraction, content control technique

Yttrium-gadolinium-aluminum garnet, activated with cerium, is widely used as a phosphor – a key component of white LEDs, serving as energy-efficient sources of white light. Depending on the content of cerium and gadolinium, the energy and spectral characteristics of photoluminescence change, and therefore the control of the content of these impurities in the powder is important. Moreover, not only the integral content of Ce and Gd is important, but also their content in particles of a certain size. In this regard, in addition to the initial powders, their fine-sized fractions isolated by the sedimentation method were studied.

The content of Ce and Gd in YGAG:Ce powders and their fine-sized fractions was monitored by means of inductively coupled plasma mass spectrometry realized in the iCAP-Qc ICP-MS (Thermo Scientific) using a reaction-collisional cell [1]. For the original powder, weights of a fixed mass of 100 mg are used, for a small-sized fraction, due to a small amount of sample, weights of about 1 mg were used (without the possibility of initial control of the exact weight of the sample). Samples were dissolved in a mixture of sulfuric and phosphoric acids at a temperature of 200 ºC using a microwave accelerated reaction system MARS 6 (CEM).

Work with small weights of about 1 mg was carried out from the assumption of a certain fraction of the matrix elements, in this case yttrium, confirmed by X-ray powder analysis. The intensity of the detected yttrium in the mass spectra made conclusions about the mass of the initial sample and the mass fraction of the remaining elements in it, respectively. The detection limit was therefore two orders of magnitude or more overestimated, but due to the high sensitivity of the method it was sufficient to analyze the content of cerium and gadolinium.

Thanks to the developed method, it was possible to study the influence of the particle size on the content of cerium and gadolinium in them, which, in the context of other results on the phosphor powder, made it possible to get a whole picture of the influence of impurities on the luminescence of YGAG:Ce powders [2], and to give recommendations on the modification of powders for improvement of white LEDs on their basis [3].

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POSSIBILITY OF DEVELOPING A REFERENCE PROCEDURE OR PRIMARY REFERENCE PROCEDURE TO ENSURE TRACEABILITY OF MEASUREMENTS FOR MERCURY IN GAS MEDIA

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Keywords: mercury, atomic absorption spectrometry, method of measurement, mass spectrometry with ICP, mercury generator, traceability

Among environmental pollutants that have negative impact on ecosystems and man, mercury takes one of the first places, due to high toxicity, fluidity, and its properties to be accumulated in the food chains of aquatic and continental biocenoses. The main method of determining mercury (in the Russian Federation) is atomic absorption spectrometry. Based on this method, more than 120 methods of measurement were developed, certified and registered in the Federal Information Fund (hereinafter FIF), among them over 20 methods for air and gas medium, including 4 for natural gas.

A wide range of measuring equipment is required to implement the method of atomic absorption spectrometry. According to FIF, there are more than 50 types of mercury analyzers in their records. Most of universal mercury analyzers and atomic absorption spectrometers are based on the “cold vapor” method and are traced to a pure substance - mercury, using reference materials of water solutions of mercury ions for graduation and calibration (more than 8 names according to FIF data). A number of gaseous medium analyzers require either a mercury vapor generator or a thermo diffusion generator combined with micro flow sources for verification and calibration of gas mixtures. In this regard, the problem to ensure the traceability of measurements of the mercury mass concentration in gaseous media, especially at levels of 10 ng / m^3, becomes essential.

Our Institute, for the first time in Russia, proposed, tested and implemented the scheme to ensure the traceability of measurements of the mercury mass concentration in gaseous media. The scheme became the base for method of measurement “Method of measurement of the mercury mass concentration in binary gas mixtures by mass spectrometry with inductively coupled plasma” No. MI-242/2-2015, Attestation Certificate No. 625/206-(01.00250) -2015, February 13, 2015. The Method of measurement were made within the framework of the development of the industry standard “Natural inflammable gas. Method of determination of mercury by atomic absorption spectrometry (cold vapor)” for Gazprom Company.

Metrological characteristics of the method are presented in the table 1.

T a b l e 1. Metrological characteristics of the method

Mercury mass concentration measurement range , (at temperature = 20 0C, pressure 101,3 kPa); µg/m3	Relative Expanded Uncertainty of measurements U^0, %
From 0,03 to 1000 (inclusive).	4

The essence of the proposed scheme is - preliminary sampling of gas mixture from the output of a generator (storage gas vessel, etc.) into a calibrated gas syringe and its analysis by mass spectrometry with inductively coupled plasma (hereinafter the ICP-MS method). The calibration of the spectrometer is carried out with saturated vapors (constant) of pure metallic mercury introduced

directly into the argon stream. The mercury content in saturated vapors is calculated with the formula:

$$C = \frac{3216522{,}61 \times 10^{-(A+[B/T])}}{T}$$

C - Mercury vapor mass concentration, ng/ml;

A - -8,134459741

B - 3240,871534

T - Absolute temperature, K

The undoubted advantage of this scheme is the potential of using various gases and gas mixtures to create a matrix medium, which influences the mercury content in analysis by other methods.

Therefore, the proposed scheme and the developed method of measurement based on the ICP-MS will provide traceability in the transfer of a unit mass concentration of mercury in gas media and will serve as the basis for creating a reference method of measurement.

DEVELOPING A CERTIFIED REFERENCE MATERIAL BASED ON PLUTONIUM DIOXIDE FOR TOTAL PLUTONIUM CONTENT

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Keywords: developing a reference material, nuclear material accounting, plutonium dioxide, coulometry, isotopic composition, mass fraction

Metrological support of measurements of chemical composition of liquid and solid substances and materials is one of the most important tasks of the present-day metrology. Nuclear industry desperately needs high-quality and reliable measurement results, because this guarantees safety. Obtaining such results is impossible without certified reference materials [1]. Previously the demand for reference materials was met by means of sectoral research institutes, a lot of which at the moment shut down this line of their activities because of various reasons. In particular, to this day certified reference plutonium dioxide materials (in terms of isotopic composition and mass fraction of the base material) are almost completely spent. However, radiochemical method of spent nuclear fuel reprocessing results in production of various high-purity products that may be the basis for reference materials.

To solve the problem of metrological support of means and methods of measuring plutonium content, Analytical Laboratory of RT-1 Plant in association with A. A. Bochvar Research Institute for Inorganic Materials (VNIINM) currently develops a certified reference Pu dioxide material with a certified value of total Pu mass fraction [2, 3].

As an initial material a batch of Pu dioxide powder was used. The powder is extracted during radiochemical reprocessing of ground spent nuclear fuel from BN and VVER reactors. Homogeneity of the batch of the reference materials was provided by the processing technology used: Pu dioxide powder was precipitated from a single vessel with the solution. The material was manufactured according to a process procedure of the enterprise and represents powder with particles of 1 to 50 μm. In the middle of a long campaign of reprocessing of SNF with a constant burn-up fraction, during which there was no impact caused by variation of certain parameters of the process, a container was selected from the batch of containers with the precipitate. To provide homogeneity in terms of isotopic composition, mixing and sampling were performed using a special device (probe).

Experimental activities with a view to defining a certified value of total Pu mass fraction were performed using a high-frequency unit, potentiostat, i.e. coulometric integrator PIK-200 (ПИК-200), designed by Ural Research Institute for Metrology (UNIIM), using a branch method [4] certified by A. A. Bochvar Research Institute for Inorganic Materials (VNIINM). Confirmatory measurements were performed using spectrophotometric analysis and K-edge densitometry.

Characteristics of homogeneity of the particulates were estimated by a method based on multiple measurements of mass fraction of the certified component in several samples randomly selected from the total volume of material with further processing of results according to a scheme of single-factor analysis of variance in accordance with [5]. Characteristics of an error caused by heterogeneity were 0.047 and were taken into consideration when evaluating the error of the certified value of a check sample.

The certified material was considered to be fit for use as a basis for preparation of a check sample for interlaboratory comparative tests among laboratories of Rosatom enterprises [6, 7].

The main targets of interlaboratory comparative tests are to confirm the specified characteristics of errors for methods used, to evaluate quality of laboratory measurements and tests, to evaluate competence of test personnel, as well as to certify a reference material using inerlaboratory certification method.

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VALIDATION OF THE TEST PROCEDURE FOR STRETCHING IN LINE WITH GOST 10446 WITH THE USE OF A REFERENCE MATERIAL OF WIRE WIRE FOR QUALITY CONTROL

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Testing laboratory must specify the ranges of characteristics from measurement procedures (tests).

However, this requirement is not always feasible due to the lack of information about the ranges of characteristics in the standardized measuring procedures (tests).

In this case, the laboratory's quality management system should regulate rules and procedures for determining the actually realizable measurement range of the methodology.

The procedure for determining the range of determination and the accuracy of the methodology is the procedure of validation.

The documented validation procedure is developed on the example of the tensile test method in accordance with GOST 10446 (ISO 6892).

The scheme of the validation process is shown in Figure 1.

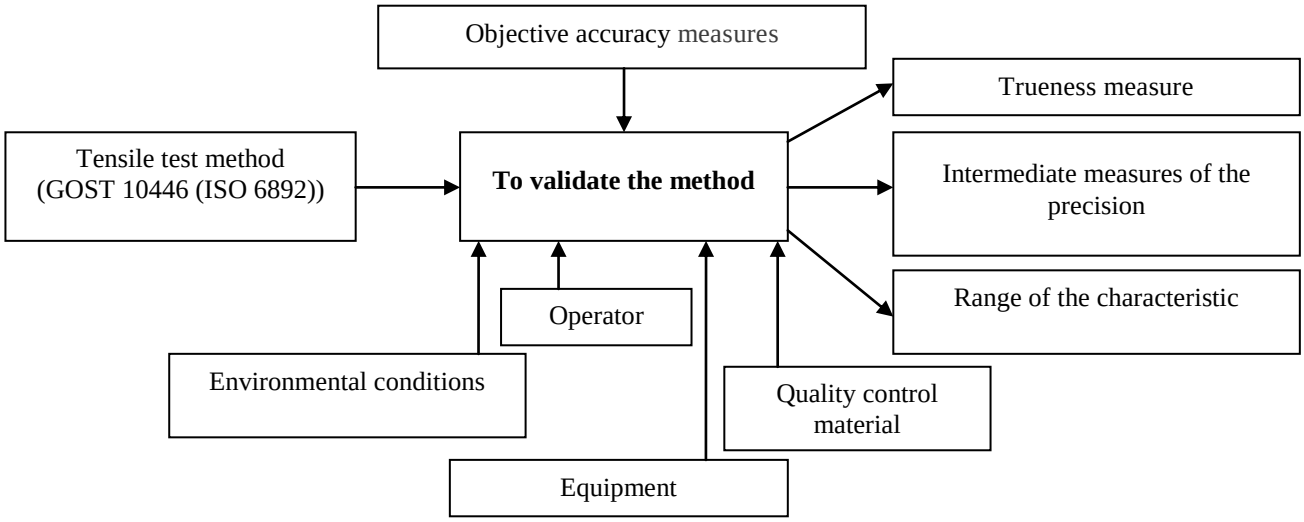

Fig. 1. Scheme of the validation process

The main validation characteristics are the following:

- the range of the characteristics definition;

- accuracy measures that have the greatest impact on the result (with validation within one test laboratory - trueness measures and intermediate measures of the precision).

During the validation, it is necessary to carry out measurements using a quality control material with a known value of the characteristic.

To assess the accuracy of the test procedure in accordance with GOST 10446, a quality control material (hereinafter - QCM) prepared by UNIIM was used, which is a reference material of a steel wire of thermally processed, normal accuracy, light, 4 mm in diameter, 200 mm long [3] with a assigned value of the characteristic “yield strength” $\tilde{A}$ = 286,24 N/mm^2 and the error of the assigned value $\Delta_{аттр}$ = 9,6 N/mm^2. The method of assigned value establishing is interlaboratory certification by [4].

The estimation of the intermediate measure of the precision $\sigma_{R_л}$ was carried out based on the results of an internal laboratory experiment [5], which consists of tests of a set of QCSs performed in the laboratory when the main influencing factors of the measurement conditions change (time, calibration, operator, equipment).

The estimation algorithm is in accordance with [5].

The estimation of the trueness measure Δ_c of the test procedure in the laboratory was carried out by estimating the laboratory bias from the adopted reference value. The certified value of QCS is used as the reference value.

The validation results of the methodology were processed through the program and formalized with a validation protocol in the form shown in Table 1.

T a b l e 1. Protocol for validation of the standardized test procedure for tensile tests (GOST 10446)

The name of the validation characteristic of the method	The established value of the validation characteristic
Trueness measure	
Intermediate measures of the precision	
Range of characteristic	

Thus, in the course of the work:

- the value and the error of the value of the reference material wire for quality control have been established;

- general methodological approaches to the development of a documented procedure “Validation of the test method” has been developed for inclusion in the quality management system of testing laboratories in order to establish ranges for the characteristics determination of the method;

- developed a program for processing data and calculating the values of validation characteristics of the method.

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DEVELOPMENT OF A CERTIFIED REFERENCE MATERIAL OF THE PHYSICAL PROPERTIES OF SOIL CLAY (LOAM)

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When carrying out engineering surveys, it is important to accurately determine the name of the soil and its main characteristics for design solutions for construction. All the soils differ from each other in many ways in accordance with [1]. The physical properties of soils are their characteristics, which describe the physical state of a particular soil, as well as its ability to change its state under the influence of various physicochemical factors.

The types and composition of laboratory determinations of soil characteristics are defined in Appendix M of SP 11-105 [2].

To control the accuracy of laboratory determinations of physical properties of soils, reference materials (RM) are needed. At present, there are no RMs of physical properties of soils in Russia, thereby LLC NPF “ISIz” and UNIIM was developed by the certified reference material (CRM) of physical properties of soil clay (loam) - GSO 11038-2018.

The metrological characteristics of GSO 11038-2018 are presented in Table 1.

T a b l e 1. Metrological characteristics of GSO 11038-2018

Certified characteristic	Unit number designation	Certified value	Limits of the absolute error of the certified value for P = 0,95, ± Δ,%
Humidity at the yield point by the balancing cone method	%	36,7	1,9
Humidity at the rolling edge	%	21,2	1,5
Density of soil particles by pycnometric method	g/cm^3	2,71	0,03

The CRM material is a powder of fineness less than 1 mm, prepared from clay (loam) soil ground, crushed and dried to an air-dry state, without organic inclusions, packaged 250 g each in hermetically sealed polyethylene bags.

The raw material for the production of CRM was a loam selected at the Reshetnikovskoye oil field, the Udmurt Republic, Mozhginsky District.

The technological preparation of the raw material included the operations necessary to ensure the homogeneity of the material.

The establishment of certified values and the estimation of the error of the certified values of the RM was carried out according to [3] by the method of interlaboratory experiment on the basis of 15 independent results obtained in testing laboratories accredited for technical competence in the national accreditation system having experience in soil research. When calculating the errors of the certified values, the results of estimating the homogeneity are taken into account.

The homogeneity was estimated in accordance with [4] using the algorithm for disperse materials.

Investigation of the stability of RM was carried out in accordance with [5] using the results of measurements obtained on the material of the experimental batch with the application of the corresponding measurement procedures by [6]. According to the results of the stability study, the shelf-life of the material is 5 years.

Development and application of GSO 11038-2018 physical properties of soil clay (loam) allows:

- to monitor the accuracy of the results of moisture measurements humidity at the yield point by the balancing cone method, humidity at the rolling edge, density of soil particles by pycnometric method, performed according to [6];
- conduct interlaboratory comparisons;
- carry out a competence check of laboratories.

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CREATION OF A SYSTEM FOR AUTOMATIC MONITORING AND ACCOUNTING OF POLLUTANT DISCHARGES INTO WATER OBJECTS

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Keywords: environmental protection, automatic monitoring of pollutant discharges into water objects, indicators of pollutant discharges, discharge monitoring and accounting system, metrological support, metrological traceability

For the purpose of the provisions of 67 Article of Federal Law of 10.01.2002 No. 7-FZ “On Environmental Protection” (as amended by Federal Law of 21.07.2014 No. 219-FZ) [1], which prescribes to organize the automatic monitoring of pollutant emissions, pollutant discharges, UNIIM conducts relevant theoretical and experimental research, takes an active part in the preparation of regulatory legal acts in the field of automatic measuring and recording instruments of indicators pollutant emissions and pollutant discharges, and also plans the development of appropriate methodological support, proposed in furtherance of the above regulatory legal acts.

The automatic monitoring system involves a complex of technical means that provide for automatic measurements and recording of pollutant emissions and/or pollutant discharges, fixation and transmission of information on pollutant emissions and (or) pollutant discharges into the state register of objects that have a negative impact on the environment.

The indicators of pollution discharges that are the subject to automatic test include the concentrations of pollutants in waste water or other indicators characterizing the quality of waste water (hydrogen index, chemical oxygen demand (COD) and (or) biological oxygen consumption), volume flow and temperature of discharged sewage, specified in ITS 22.1-2016 [2] and (or) in ITS BAT for a particular industry [3-5].

The need to develop the metrological support for automatic measuring and recording instruments of indicators pollutant emissions and pollutant discharges is dictated by the requirements of Federal Law of 26.06.2008 No. 102-FZ “On Ensuring the Uniformity of Measurements” [6], since issues related to the implementation of activities in the field of environmental protection, as well as measurements in the field of environmental protection, to which the mandatory metrological requirements are established, are related to the sphere of state regulation of ensuring the uniformity of measurements. Therefore, the creation of an automatic monitoring system and its operation are carried out in accordance with the requirements established by the legislation of the Russian Federation on ensuring the uniformity of measurements [6], and the requirements of the technical documentation of the manufacturer of the measuring instruments used.

At all life-cycle phases, from the creation of an automatic monitoring system to its direct operation, there are stages requiring appropriate metrological support. These include survey and design works, conducting of pre-commissioning, measurements carried out during the pilot operation, as well as during the confirmation of the correctness and quality of the automatic monitoring system.

The development of the metrological support for the automatic monitoring systems takes into account the specificity of their functioning, which consists in combining two types of measured values: physical and chemical measurements of the content of pollutants, as well as volumetric and (or) mass flow. The combination is carried out using specially developed measurement procedures for integral characteristics of pollutant discharges and related software that takes into account the

features of the received measuring information and generates the reporting on the current and integral indicators of the sewage composition. The metrological support for the automatic monitoring systems is planned to be built on the basis of provisions of GOST 8.596-2002 [7].

UNIIM for experimental investigations on its own initiative is developing a reference complex allowing to reproduce the processes of automatic monitoring and recording of pollutant discharges into water objects (AISKKV).

AISKKV has the following applications:

− conducting of calibration (verification) of industrial continuously-operated analyzers, designed to test the properties and composition of water;

− carrying out of tests for the approval of the type of automated measuring systems for industrial environmental monitoring of discharges;

− simulation of the discharge point, design of systems of industrial environmental monitoring of discharges and report preparation about the results of its implementation;

− development, testing and production of reference materials.

AISKKV includes the following equipment:

– a closed circuit on the basis of a pouring installation with circulating water, equipped with a single trunk for placing of analyzers and sensors for monitoring of the properties and composition of water, secondary converters;

– an equipment for water circulation (pumps, flowmeters);

– an equipment for measuring of flow, temperature, pressure and mass (volume) of water in the circuit;

– an equipment for collection, processing and transmission of data;

– other equipment necessary for the functioning of the system.

The measured physicochemical parameters of water in AISKKV are given in Table 1.

T a b l e 1. The measured physicochemical parameters of water in AISKKV

Analyzed indicators	**Features of measurements**	
Hydrogen index pH, pH units	potentiometry	Continuous mode sensors
Oxygen, mg/L	luminescence	
Conductivity, μS/cm	conductometry	
COD, mg O/L	determination of bichromate oxidability in accordance with GOST 31859-2012 [8]	Analyzers with automatic sampling system, analysis time is not more than 45 minutes
Phosphate-ion, mg/L	colorimetric	
Ammonium ion, mg/L		
Nitrite-ion, mg/L		
Nitrate-ion, mg/L		
Water temperature, ^{o}C	potentiometry	Continuous mode sensor

Primarily it is planned to test the reference complex for monitoring and recording of pollutant discharges on objects of centralized drainage systems of settlements and urban districts. The list of pollutants in respect of which mandatory automatic monitoring is performed is determined on the basis of the capacity of treatment plants, which is provided in ITS 10-2015 [9].

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ESTIMATION OF MATERIAL PREPARATION QUALITY OF CERTIFIED REFERENCE MATERIALS OF SOLID WET SUBSTANCES

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Keywords: certified reference materials, quality of material preparation, estimation of uncertainty due to inhomogeneity of wet solid substances

The requirements for additional justification for the application of the ANOVA method recommended in the ISO Guide 35:2017 [1], during inhomogeneity estimation of solid wet substances, are shown in [2] using material-destroying methods. Often such destructive methods are used in determining the mass fraction of moisture in solid materials [3-5]. The mass fraction of moisture is one of the most unevenly distributed in terms of volume indicators, therefore, it was chosen to study the features of certified reference material preparation (hereinafter - CRM) of solid substances.

In this study, for the case of CRM of moisture mass fraction of in solid substances characterized by the thermogravimetric method, the models of the random parameter (normal distribution, with the detected influencing factor, the results of the measurements are independent) and random walk (normal distribution, with detectable influencing factor, measurement results are dependent) are described.

Features of processing and interpretation of the measurement results of the moisture mass fraction described by the models [2] using the Monte Carlo method [6] are shown in Fig. 1: simulated measurement results (a), estimates of the current total mean (b), standard deviation and standard deviation mean (c).

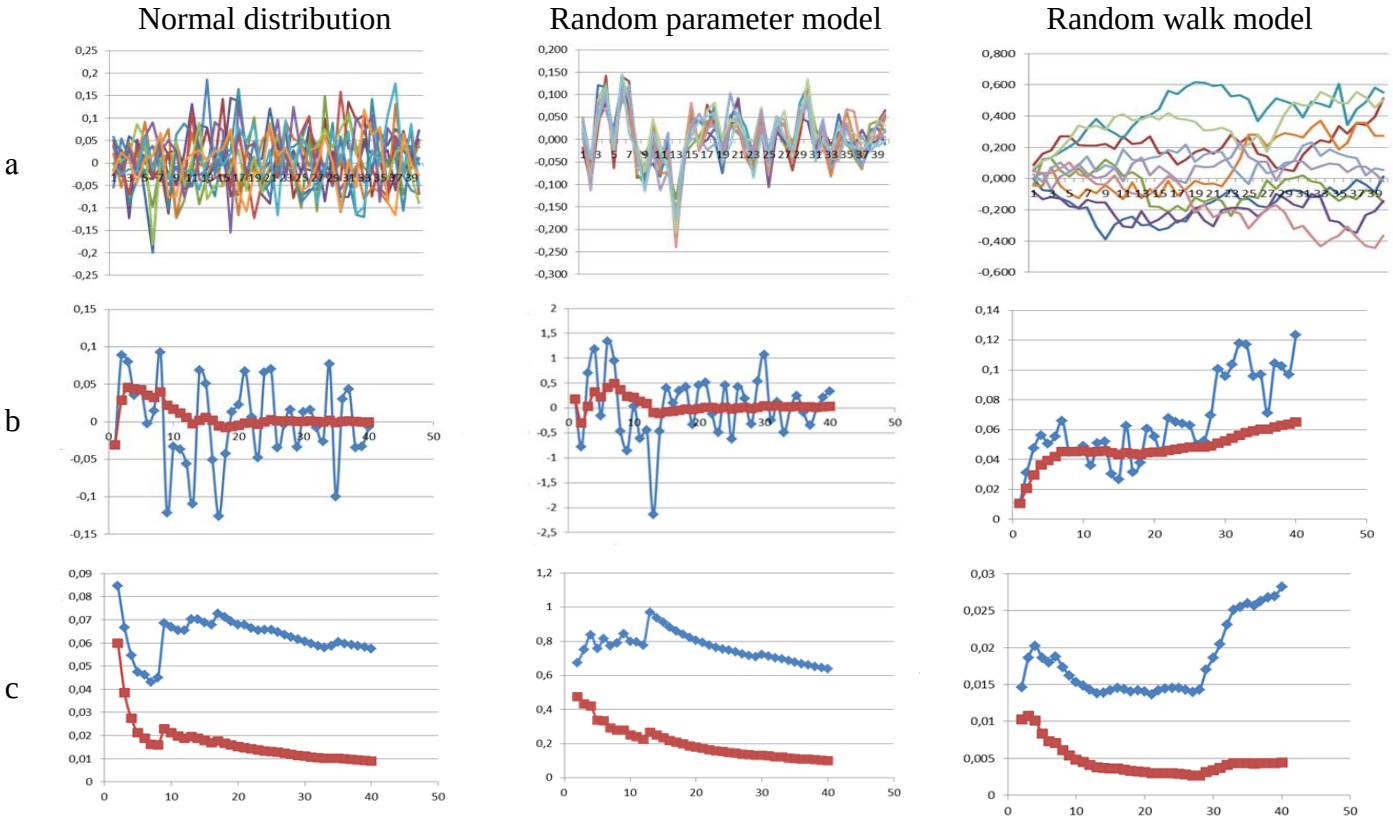

Fig. 1 . Features of processing and interpretation of the measurement results of moisture mass fraction described by the proposed models

T a b l e 1. Summary data for precision characteristics determination of the simulated measurement results by the proposed methods and using ANOVA method

Data sets	ANOVA		Random parameter model		Parameters for Monte Carlo simulation	
	$RMSD_{inhomog}$	$RMSD_{method}$	$RMSD_{inhomog}$	$RMSD_{method}$	$RMSD_{inhomog}$	$RMSD_{method}$
A data set that corresponds to a random parameter model	0,045	0,026	0,031	0,020	0,050	0,025
A data set corresponding to the random walk model	0,090	0,057	0,050	0,021	0,050	0,025

As can be seen in fig.1 in the case of the effects described by the random walk model, the values of the current mean square deviation of the average measurement results increase with increasing the number of experiments. We obtain overestimated values of the characteristics of CRM (Table 1), using ANOVA method for such a set of measurement results, which can lead to errors in characterization (for example, an incorrect estimate of the mean, an incorrect estimate of the inhomogeneity).

Tables 1 and 2 show the results of the RMSD that characterize the inhomogeneity - ($RMSD_{inhomog}$) and RMSD caused by the applied measurement procedure ($RMSD_{method}$).

Then, the possibility of using the proposed approach for processing and interpreting the experimental data was confirmed. Measurement results of moisture mass fraction in candidate-materials to CRM were used: wheat flour and coal. At the stage of estimating the material inhomogeneity and establishing the certified value, five series of eight consecutive measurements by the thermogravimetric method were obtained. The table presents the results of the standard deviation that characterizes the inhomogeneity and standard deviation caused by the applied measurement procedure.

T a b l e 2. Summary data for precision characteristics determination of the experimental data by the proposed method and ANOVA method

Material (substance) - candidate to CRM	ANOVA		Random walk model	
	$RMSD_{inhomog}$	$RMSD_{method}$	$RMSD_{inhomog}$	$RMSD_{method}$
Wheat flour	0,012	0,015	0,011	0,013
Coal	0,075	0,060	0,050	0,050

As can be seen in table 2 measurements results of moisture mass fraction in coal are unsuitable for characterization, since the effects of correlation of single results are revealed, possibly due to draw back of procedures in selecting the sample for analysis from the prepared total volume, which in turn leads to the accumulation of errors and the growth of RMSD from inhomogeneity, among others.

In future the analysis of heterogeneous substances (materials) with the help of destructive methods, it is proposed to introduce a separate stage of research, the essence of which is: verification of the set of experimental data for the effects described by the random walk model, including

treatment by the classical ANOVA method, as well as calculation of the Kolmogorov structural function for random walk models. The inconsistency in the estimates indicates the disadvantages of the sampling procedure for multiple samples, or the draw backs in preparation of samples.

Thus, in the case of heterogeneous material of certified reference material and application distractive methods in its characterization additional justification of ANOVA method is necessary.

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ON THE DEVELOPMENT OF REFERENCE MATERIALS OF FOOD QUALITY INDICATORS

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Keywords: food products, quality improvement strategy, safety indicators, quality indicators, identification indicators, state measurement standard, metrological traceability, reference material, measurement procedures

Since the adoption in 2000 of Federal Law “On the Quality and Safety of Food Products” [1] and in 2002 of Federal Law “On Technical Regulation” [2], the issue of safety of food products and food raw materials was in the foreground. All products supplied to the consumer had to satisfy the mandatory requirements regulated in the relevant Technical Regulations of Russian Federation and Customs Union (TR CU) [3-12]. In particular, TR CU introduced the permissible levels of toxic products, mycotoxins, antibiotics, growth stimulants, pesticides, radionuclides, microbiological safety indicators, the excess of which poses a potential threat to human health and life. The requirements for product quality set out in the technical conditions standards became voluntary. The conducted policy allowed reducing the statistics of poisoning and death due to the use of unsafe food products, but led to the appearance of a significant share of products with low consumer properties, including falsified products. This policy allowed to reduce the statistics of toxication and death due to unsafe food products, but led to the appearance of a significant proportion of products with low consumer properties, including falsified products.

To war against the described negative trends in 2016 an Executive Order of the Russian Federation Government approved a “Strategy to Enhance Food Quality in the Russian Federation until 2030 (hereafter the Strategy)” aimed to “ensure adequate nutrition, disease prevention, increased longevity, and a higher quality of life and to promote the production and marketing of proper, high-quality food” [13]. In framework of implementation of the Strategy the Federal Agency for Technical Regulation and Metrology (Rosstandart) was assigned to conduct a plan of actions to create and develop metrological support for physical and chemical measurements in food industry. Analysis of the current TR CU in the field of food products [3-12] has identified a number of disadvantages, including the limitation of nomenclature of reference materials (hereafter CRMs), both in terms of food safety indicators and quality indicators, as well as the lack of metrological traceability of majority of CRMs to State primary standards currently functioning in Russian Federation in the field of physical and chemical measurements. In this regard UNIIM was tasked to develop the CRMs of composition and properties of food products.

The first stage of development consisted in drawing up the nomenclature of materials for CRMs and the list of certified characteristics. The choice was made in the following sequence. The several stable and homogeneous matrices representing the entire range of products covered by TR CU were selected for each of the current TR CU. So, for example, for TR CU 015/2011 “On Safety of Grain” [3] we chosen wheat, rye, rice, oilseed meal, feed-stuff as materials for CRMs; for TR CU 033/2013 “On Safety of Milk and Dairy Products” [9] - milk powder (whole, skim), dairy mix, freeze-dried curd and sour cream, dry cheese; for TR CU 034/2013 “On Safety of Meat and Meat Products” [10] - freeze-dried meat and egg powder, etc. Next, we selected the main indicators for the selected products as characteristic representatives of the product groups. Taking into account the reference base available at UNIIM, the following order of release of CRMs was established:

1) CRMs with certified values of indicators of identification and nutritional value (moisture, nitrogen, protein, fat, ash, calcium, phosphorus); 2) CRMs with certified values of safety indicators (content of mercury, arsenic, lead, cadmium).The absence in the proposed line of matrix CRMs, certified for the content of mycotoxins, benzapyrene, pesticides, polychlorinated biphenyls, is explained by the specifics of the analytical methods and measuring instruments used to determined the concentrations of the listed substances. The control of their content in food and food raw materials requires the calibration of measuring instruments with pure substances or their solutions. Consequently in this case the presence of CRMs of the composition of pure substances is necessary.

Metrological traceability of the certified values of quality indicators in developed CRMs of food composition is provided through measurements using the following standards:

- 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), which in its turn has metrological traceability to units of values reproduced by The State primary standard of mass (molar) fraction and mass (molar) concentration of component in liquid and solid substances and materials on the basis of coulometry GET 176-2017.

In addition, it is planned to conduct research of materials for CRMs using a UV-visible spectrophotometer and a digital refractometer.

In carrying out work on tests of CRMs in order to type approval it was also planned to develop two primary reference measurement procedures. The first developed procedure is designed to perform high-precision measurements of the fat mass fraction in food products and food raw materials using the improved Randall extraction method. The method is based on quantitative extraction of free and bound fat from product samples with subsequent weighing. The method is implemented with a preliminary stage of hydrolysis for all kinds of samples, except for feed-stuff and wheat grain. The second primary reference measurement procedure is designed to perform high-precision measurements of ash content in food products and food raw materials. The method is based on burning the product sample with the subsequent calculation of the mass of the fireproof residue.

For today the staff of 241 laboratory of UNIIM has performed the following works:

– based on the successful results of tests CRMs of dry milk products (set ASM-2 of CRMs UNIIM) were included into the State Register of Approved Type Reference Materials of the Russian Federation under the numbers GSO 11086-2018 / GSO 11091-2018 (6 types);

– tests have been completed for CRMs of composition of baby food products - grain dry porridges for nutrition of babies (4 types) and grain-milk dry porridges for nutrition of babies (4 types);

– experimental studies of the primary reference measurement procedure of the fat mass fraction in food products and food raw materials have been conducted and the procedure preparation of the measurement procedure for submission to Rosstandart in accordance with [14] has been completed.

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REFERENCE MATERIALS OF THE RUSSIAN FEDERATION: STRATEGY OF ENSURING THE UNIFORMITY OF MEASUREMENTS UNTIL 2025

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The issues of development, testing, approval and use of reference materials (RMs) in the Russian Federation currently have a high degree of relevance. This is due to modern trends in metrological support of measurements (CIPM MRA, new version of ISO/IEC 17025 “General requirements for the competence of testing and calibration laboratories”, ISO 17034 “General requirements for the competence of reference material producers”, etc.), legislation of the Russian Federation in in the area of ensuring the uniformity of measurements, laboratory accreditation criteria, legal entities, individual entrepreneurs, conducting work and/or rendering services on ensuring the uniformity of measurements, providers of interlaboratory comparison tests, in force in our country. No wonder, that in the Strategy of ensuring the uniformity of measurements till 2015, approved by the Government order, a crucial role is assigned to issues, relating to RMs and to the creation of the necessary RM nomenclature

The key international documents, to be used in the development, production and application of reference materials, are developed by Committee on reference materials (ISO/REMCO) of International organization for standardization (ISO) and by International organization of legal metrology (OIML). During the last five years in the framework of the National system of the Russian Federation systematic work is underway on the harmonization on national documents on standardization with the generally recognized international documents.

Reference materials of the following categories are currently available in the Russian market:

- reference materials of approved types (GSO), branch RMs (OSO) and in-plant RMs (SOP), constituting the bulk of RM market in Russia. And the proportion of GSO is about 40 %. In the sphere of the state regulation of ensuring the uniformity of measurements only RMs of approved types may be used.

- interstate reference materials (MSO) and COOMET RMs. The share of sales of these RM categories in Russia is insignificant. In the Registers of MSO and COOMET RMs the proportion of RMs, produced in foreign countries (mainly national RMs of Ukraine, Republic of Kazakhstan, Republic of Belarus), is not more, than 20 % (the rest are national GSO) At the same time, according to the provisions of the Federal Law No. 102-FZ “On ensuring the uniformity of measurements”, despite the interstate status recognized by our country, foreign RMs of these categories cannot be used in Russia in the spheres of the state regulation in the area of ensuring the uniformity of measurements without conducting a range of works on their recognition as RMs of approved types.

- RMs of foreign issue. The proportion of foreign RMs, registered as RMs of approved types in the Register of approved RM types is extremely low, about 18 % and most of them are produced in the CIS countries. Accordingly, the possibility of using such RMs in the system of ensuring the uniformity of measurements is extremely insignificant. Imported RMs are mainly used in the spheres, not covered by the spheres of the state regulation in the area of ensuring the uniformity of measurements (pharmaceuticals, clinical diagnostics, doping control and some others), for which there are no national RMs in Russia.

Along with the above listed categories according to international documents RMs are issued as certified RMs (certified reference materials) and RMs (reference materials), the requirements for which and possibilities of using are different. In the meantime the market of RMs in the Russian Federation is a symbiosis of all RM categories. The system of the state regulation covers only one of RM categories (namely, RMs of approved types - GSO), the rest of the market of RMs remains open and issues of RM manufacture, quality, and use are not controlled in any way. Of course, this adds confusion to the possibilities of RM using and often misunderstanding on the part of RM users in matters of what, when, in what field of measurements it is possible and necessary to use.

Modern activities in the field of metrological support of measurements in the Russian Federation are closely related to the acute, and sometimes extremely urgent need to address a number of priority tasks:

- solution of the problem of import dependence in RMs, that is why the issue of the development of the forecasting system for the needs in RMs, planning of RM creation in the country becomes urgent;

- further systematic improvement and harmonization with international requirements in the field of RMs of the national regulatory legal framework that facilitates the development and use of national RMs, complying with modern requirements, while taking into account the peculiarities of the national system of the state regulation in the area of ensuring the uniformity of measurements;

- development of information support system in the area of RMs, relating not only to RMs of approved types, but to reference materials of other categories, presented in national market.

The need to establish the system of QMS conformity assessment for national RM producers with the requirements of ISO 17034 “General requirements for the competence of reference material producers” remains an extremely important issue.

On the whole, according to the authors, the Strategy for ensuring the uniformity of measurements in the Russian Federation till 2025 sets urgent and priority tasks, and the goals, claimed by the Strategy are quite achievable, provided the system of the state regulation in the field of reference materials is improved in the consolidation with the metrological community.

EVALUATION OF UNCERTAINTY OF THE CERTIFIED VALUE OF MULTICOMPONENT REFERENCE MATERIAL

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Keywords: multicomponent reference material, uncertainty of RM certified value, RM characterization by the method of preparation

RMs of multielement solutions are widely used in modern quantitative chemical analysis in the construction of calibration dependences of output signals, for example spectral measurement instruments, on content of determined components. The convenience of using such RM is characterized by the universality of modern instrumental methods of analysis, which allows calibration for several elements at once.

For the characterization of multicomponent RMs by the preparation procedure ISO GUIDE 35 suggests using weighted averages estimates [1, 9.3.4]. In this case the content of component in the mixture of substances - $\bar{x}_w$ is determined as $\bar{x}_w = \sum_{i=1}^{N} w_i x_i$, where x_i is a measured value of content of the i[th]-component of the initial substance with covariances - $u(x_i, x_j)$, $w_i = m_i / \sum_{i=1}^{N} m_i$ are weight coefficients, m_i is a measured value of mass of i[th]-initial substance in mixture of substances by mass $m = \sum_{i=1}^{N} m_i$ with covariances $u(m_i, m_j)$, $i, j = \overline{1, N}$.

ISO GUIDE 35 also suggests the formula for estimation of standard uncertainty due to characterization by the procedure of gravimetric preparation a binary mixture [1, (13)], when $N = 2$.

However, in the framework of the GUM metrology [2] in [3] is shown that the square of the total standard uncertainty of the output quantity - $\bar{x}_w$ can be represented for unlimited number of components in general form

$$u^2(\bar{x}_w) = \frac{1}{(\sum_{i=1}^{N} m_i)^2} \sum_{i,j=1}^{N} [m_i m_j u(x_i, x_j) + (x_i - \bar{x}_w)(x_j - \bar{x}_w) u(m_i, m_j) + (x_i - \bar{x}_w) m_j u(x_i, m_j)] \quad , (1)$$

where $u(\bar{x}_w)$ is the total standard uncertainty of the $\bar{x}_w$,

x_i and m_i is the result of measurements.

Let us consider the application of (1) in characterizing by the way of preparation of RM of multicomponent mixture of metals in the form of a solution from the characterized metal solutions with the known values, uncorrelated values x_{ki} - content of the k[th]-metal in i[th]-solution with mass m_i with uncertainty $u(m_i)$, with appropriate known uncertainties - $u(x_i)$, $k = \overline{1, K}$, $i = \overline{1, N}$. The solution will be characterized by the content of the solvent component x_{0i} in the i[th]-solution. Then the content of the k[th]-metal and the solvent component solution in the mixture of N solutions - $\bar{x}_{kw} = \sum_{i=1}^{N} w_i x_{ki}, k = \overline{0, K}$. If all measurements x_{ki} and m_i are carried out independently and the

mixture of metal solutions is considered homogeneous, then k[th]-component of the mixture (1) becomes

$$u^2(\bar{x}_{kw}) = \sum_{i=1}^{N}[m_i^2 u^2(x_{ki}) + (x_{ki} - \bar{x}_{kw})^2 u^2(m_i)] / (\sum_{j=1}^{N} m_j)^2 ,\ k = \overline{0, K} . \quad , (2)$$

Expression (2) allows to estimate separately the contributions to the estimation uncertainty of the $\bar{x}_{kw}$ due to the uncertainties in the measurement of the contents of components and masses of the initial solutions.

Comparison of the proposed approach and modelling by Monte Carlo method [4] is carried out by processing the results of the characterization of multi-element RM, which is a mixture of solutions of chemical elements (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd) in a 5 % nitric acid. The content of each certified component in each solution and the weight of aliquots with the appropriate total standard uncertainties were taken into account.

For estimation of certified values of the content of elements in the mixture the weight average value of the mass of each individual component was determined by (1), and the associated standard uncertainty was determined by (2).

For estimation the same parameters by the Monte Carlo method, modelling was conducted of $1 \cdot 10^6$ values of the content of each element with normal distribution of input quantities with a standard deviation numerically equal to their total standard uncertainty.

The comparison showed the compatibility of the obtained estimates and, consequently, the correctness of the weighted average values of the content of the components in the mixture and calculations of their standard uncertainty by (1). At the same time , it is shown that the most significant contribution to the uncertainty of the certified values is introduced by the uncertainty of the mass proportions of the tested components in their initial solutions (relative contribution greater than 90 %), which is characterized by the composition of gravimetric preparation constituents of pure substances, which is characterized by the scheme 100 % minus the sum of impurities, the stability of these solutions and the results of comparative measurements by atomic-emission spectrometry with inductively coupled plasma (AES ICP).

Estimates of the content of components obtained by the preparation procedure are confirmed by measurements of these values by the AES ICP method (x_l, $L=2$). The final result can be considered as the weighted average of these estimates (x_r) with weighting coefficients associated with their standard uncertainties (u_l) and the square of the total standard uncertainty of the value x_r:

$$x_r = \sum_{l=1}^{L} \frac{x_l}{u_l^2} \Big/ \sum_{l=1}^{L} \frac{1}{u_l^2}, \quad , (3)$$

$$u_{x_r}^2 = 1 \Big/ \sum_{l=1}^{L} \frac{1}{u_l^2} . \quad , (4)$$

This approach is generally similar to the approach, which is used by NIST specialists in the characterization of monoelement RMs [5, 6], where certified value is obtained as the weighted average of the results of gravimetric preparation of a solution from a high-purity compound with an established content of the main component and the results of the analysis by the AES ICP method with calibration by four independently prepared “primary standards” (in the original: four primary standards) prepared from a high-purity compound with an established content of the main component.

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EXPERIENCE IN IMPLEMENTATING A QUALITY SYSTEM OF THE ORES AND ROCKS REFERENCE MATERIAL PRODUCER IN MINSTANDARTS

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Keywords: quality management system, producer, reference material, rocks, ores

Over recent years, demand for reference material has increased significantly in the mining industry. In the best Soviet times, the base of reference materials of elemental and phase composition of mineral raw materials included about 400 types, including mineralogical collections. Nowadays, there are about 850 types of reference materials in Industry Register of the Reference Materials. Most of reference materials in Industry Register of the Reference Materials have expired. For comparison: the base of reference materials of foreign producer Ore Research & Exploration Pty Ltd is more than 1000 items.

Demand for new reference material of a higher quality increases as a result of both improving the accuracy of measurements and the need for more accurate and reliable data within scientific and technical disciplines. The main idea of ISO 17034:2016 is that it is the reference material producer that undertakes to ensure the quality of reference material. The Russian version is GOST ISO Guide 34-2014.

Certified reference material is produced and certified in accordance with GOST ISO Guide 35-2015, GOST 8.315-97, GOST 8.531-2002, GOST 8.532-2002, GOST R 54500.1-2011, GOST R 54500.3-2011, GOST R 54500.3.1-2011, GOST R ISO 16269-6-2005, R 50.2.058-2007 and R 50.2.031-2003. Also, additional requirements are established in Industrial Standard 41-08-268-04 and GOST 27872-88.

It was necessary to determine the main quality parameters of the ores and rocks reference material as manufactures for implementing the Quality Management System. Systematization was carried out and set the following parameters: functional, safety, transportability, economy and aesthetic. Functional parameters are type of ore, matrix composition, constituent, certified values, uncertainty of the certified value, metrological traceability, homogeneity, stability, particle-size distribution. The main characteristic of transportability is short-term stability. Safety data for humans and the environment depend on the properties (radioactivity) and the chemical composition of the raw material. Besides, aesthetic parameters (exterior appearance) are important for consumers of manufactures.

The production factors influencing the final quality of reference material were determined.

The main groups of factors are: raw material, manufacturing process, resources, staff, the competence of the laboratories which participated in the program to characterize property value of a reference material, and the number of laboratories.

The characterization of reference material achieve by inter-laboratory test. For understanding the competence of laboratories, a procedure has been developed for assessing the rating of a particular laboratory for each type of ore and for testing each element. Based on the results of the laboratory's data, a general laboratory rating is calculated and laboratory ratings for specific testing.

Quality Management System of the ores and rocks reference materials producer in accordance with GOST R ISO 9001, GOST ISO Guide 34-2014, GOST ISO Guide 35-2015 was created and setting up in STC “MinStandarts”. By STC “MinStandarts” was developed a set of

standardized procedures of the production of reference materials (STP), which consist of 19 procedures.

Many improvements were made at the time of setting up the Quality Management System in STC “MinStandarts”. These have had a positive impact on the functioning and the activities of STC “MinStandarts”. The number of produced reference materials increased from 7 types in 2013, to 102 types in 2018.

Reference material producer STC “MinStandarts” was accredited in accordance with the requirements of International Standard ISO Guide 34:2009 by accreditation body AAC “Analitica”.

NEW CERTIFIED REFERENCE MATERIALS OF LIQUID VISCOSITY

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Keywords: reference materials, VNIIM standard materials, verification, State primary measurement standard, viscosity, research

Ensuring the uniformity of measurements of the viscosity of liquids is one of the most important conditions for socio-economic development country and scientific and technical progress, provides the basis for fair trade in domestic and international markets, which is especially important in the conditions of toughening of requirements to accuracy of evaluation quality and considering the number of natural energy sources.

In view of the fact that a large number of measuring instruments, allows you to determine the viscosity of liquids in the temperature interval from minus 35 °C to 150 °C are used in the petroleum and petrochemical industries falling within the scope of state regulation of ensuring the uniformity of measurements, of measuring instruments data must pass primary, periodic, extraordinary, inspection or verification expert [1].

In turn, the verification of the measuring instruments viscosity involves the use of such means of verification as reference materials of liquid viscosity (RM).

Used in the calibration RM should be included in the State register of reference materials of the Russian Federation, have established the metrological characteristics and to be suitable for use in a predetermined temperature interval.

Currently in Russia there are RM of liquids viscosity, the certified range of values of viscosity of 1,3 mPa·s (mm^2/s) to $1,0 \cdot 10^5$ mPa·s (mm^2/s) and in the temperature interval from 20 °C to 100 °C, with a relative expanded uncertainty with the coverage factor k=2, $U_{o\eta(v)}$:

• 0,2 % – in the range of viscosity from 1,3 mPa·s (mm^2/s) to 30 000,0 mPa·s (mm^2/s);

• 0,3 % – in the range of viscosity from 30 000,0 mPa·s (mm^2/s) to 1,0·105 mPa·s (mm^2/s).

Stability and homogeneity RM of liquids viscosity, certified temperature intervals from minus 35 °C to 20 °C and from 100 °C to 150 °C in the Russian Federation are not produced [2].

The aim of this work is development and research RM of liquid viscosity, certified temperature intervals from minus 35 °C to minus 5 °C and from 100 °C to 150 °C.

To achieve **this goal**, the following objectives were formulated:

- define the technical and metrological requirements for liquid viscosity RM, in the temperature intervals of certified from minus 35 °C to minus 5 °C and from 100 °C to 150 °C;
- identify materials from which RM will be manufactured;
- identify a set of equipment designed for research and validation, developed RM;
- to conduct a study aimed at establishing the metrological characteristics, developed RM;
- develop the technical documentation necessary for the tests for the approval of the type developed by the RM.

Technical and metrological requirements to develop RM of liquids viscosity appraise in temperature intervals from minus 35 °C to minus 5 °C and from 100 °C to 150 °C were determined by analysis of modern means of viscosity measurements and are described designed in accordance with [3, 4] technical specification and technical conditions.

Taking into account given in the terms of reference and technical specifications of requirements was made analysis of existing mineral and synthetic oils having Newtonian flow

regime. Next, at nominal values of viscosity at various temperatures, it was conducted seven selection certain types of oils and mixtures thereof, and then determine their actual values of the kinematic and dynamic viscosity, reported in Table 1.

T a b l e 1. The results of determining the actual values of viscosity

The name oil / mixture	Average measured values of dynamic and kinematic viscosity					
	mPa·s					mm^2/s
	Temperature measurement, °C					
	-5	-5	-5	-5	-5	-5
Synthetic oil 40	1470	4300	13780			
Synthetic oil 60	2055	4997	16686			
Synthetic oil 30	614			8172	15625	
Synthetic oil 30A			3563	7220		
Semi-synthetic oil 40	727			6565		
Mixture of mineral oils 10						22,1
Mixture of mineral oils 30						42,6
Mixture of mineral oils 60						62,3
The relative expanded uncertainty of the measured values of viscosity of oil/mixture, with the coverage factor k=2, $Uo\eta(v)$ = ± (0,2…2,0) %.						

After analyzing the measured values of viscosity of the studied oils, it was decided to create five RMs:

• two RMs appraise in the temperature range below 0 °C: REV-10000-1 and REV-20000-1 based on synthetic oils;

• three RM, the appraise in the temperature range above 100 °C: REV-10000, REV- 30000 and REV-60000 based on mixtures of mineral oils.

Establishment of metrological characteristics of the developed RM in the temperature interval from minus 35 °C to 150 °C was carried out on the developed, in the implementation of measures to improve GET 17-96, the reference of instruments.

Develop documentation for inclusion in the registry of the Russian Federation of reference materials produced in accordance with the requirements of [3, 6, 7, 8].

Study of the metrological characteristics REV-10000-1 and REV-20000-1 was carried out to the full extent of the normative documentation.

Investigation of the metrological characteristics of REV-10000, REV-30000, REV-60000 was conducted on an abbreviated program, as they are already included in the State register of reference materials of the Russian Federation, in the temperature interval from 20 °C to 100 °C [3].

In the investigation it was determined the metrological characteristics of the developed RM, namely: certified values of the viscosity, the relative expanded uncertainty of the certified values, and studied the homogeneity inside the sample instance and between instances in the party, short and long term instability.

The developed and investigated RM, attestation in the temperature intervals from minus 35 °C to minus 5 °C and 100 °C to 150 °C allow to solve the problem of lack of funds, verification and calibration of the viscosity measurements in these temperature ranges, and can be used during the tests in order to type approval, metrological certification with viscosity measurement techniques and error control of measurement techniques in the course of their application.

The developed RM can be used in comparisons and calibration of measurement standards as liquids-comparators.

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PERSPECTIVES OF DEVELOPONG REFERENCE MATERIALS OF THERMODYNAMIC PROPERTIES FOR METROLOGICAL SUPPORT IN THE FIELD OF THERMAL ANALYSIS AND CALORIMETRY IN THE RUSSIAN FEDERATION

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Keywords: reference materials, thermal analysis, specific enthalpy, specific heat, heat of phase transitions

Reference materials (RMs) of thermophysical properties are a traditional means of ensuring the unity of measurements in various types of thermal analysis. Temperature and enthalpy (heat) of phase transformations, specific heat, thermal diffusivity and thermal conductivity are the main parameters measured in the thermal analysis of various substances. Calibration and verification of temperature and enthalpy measuring instruments are conducted by RMs of temperature and heat of fusion. It is necessary to have different types of RMs based on materials differing in temperature and phase transitions enthalpy.

The leading companies that manufacture thermal analysis measuring instrument offer their users a wide range of tools for calibration and graduation of measuring cells made from different materials. For example, the list of calibration samples of the world leader in the production of thermo-analytical equipment Netzsch Geratebau GmbH (Germany) includes 24 names and covers practically the whole range of temperature and unit enthalpy. It includes both metals and nonmetals - 12 names of each type.

9 types of RMs of thermal physical properties (SOTS) based on corundum, potassium chloride, stainless steel, gallium, indium, tin, zinc, antimony and molybdenum have been developed at UNIIM.

Comparison of UNIIM RMs characteristics with foreign RMs [1,2] shows the location of RM certified characteristics within the claimed measurements uncertainties. UNIIM has been developed manufacturing technology of RMs that meets the requirements of customers for the shape and weight of RMs and it ensures uniformity and stability of the certified characteristics. UNIIM is the competent manufacturer of SOTS which are equipped with metrological services of more than 200 enterprises. Nevertheless, at the present time there are grounds for expanding RM nomenclature. It will allow further development of the transferring units system from primary measurement standards to measuring instruments during testing, verification, calibration of measuring instruments, certification of measurement procedures (measurement methods).

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PROBLEMS OF REFERENCE MATERIALS OF BIOLOGICAL MEDICINAL PRODUCTS

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Key words: reference materials for evaluating quality of biological medicinal products, certification of biological reference materials, procedure validation, validation parameters

Development, manufacturing and quality control of medicinal products (MPs), including biologicals, should meet specific requirements set out in the WHO recommendations, Good Practices (GxP), for instance, GMP, GLP, GPhP, etc, that have been adopted on the international, interregional, and national levels. In the Russian Federation control of medicinal products is fulfilled in line with the State Pharmacopoeia [1] and procedures provided in the relevant regulatory documentation, i.e. pharmacopoeial methods with the use of reference materials (RMs), including industrial materials, which at present should be referred to as pharmacopoeial [2, 3]. Thus, the quality of MPs is regulated by the State Pharmacopoeia, not by the national standards (GOST), therefore reference materials require their own regulatory methodological basis in the sphere of circulation of medicines, which should be based on the WHO and ICH recommendations [4-7], expert background in the sphere of certification of biological and pharmaceutical RS [8-11], and also in line with the Russian laws and regulations concerning the State Reference materials [12, 13].

According to the Federal Law "On uniformity of measurements" (FZ-102) [13] there is a hierarchical system of RM certification in Russia, which applies, first of all, to reference materials of physical quantities that are measured in units in SI system. The existing system is based on the use of certified (qualified) procedures and assessment of error as a sum of systematic and random error components [14]. This approach can be applied to measurement procedures that comprise a very small part of pharmacopoeial methods. These include procedures for determination of osmolarity, electrical conductivity, refraction index; and measurement procedures that do not require sample preparation: determination of pH, optical density, degree of coloration of liquids (spectrophotometric method), degree of opalescence (turbidimetric method), density, viscosity, and specific optical rotation [15]. Other pharmacopoeial methods require a special approach.

The most important feature of biologicals is the following: RMs only with a procedure, in which it is used (not only RM), is the instrument of transfer of measurement units; these procedures are empirical and generally require sample preparation of different degrees of complexity [10].

Consistent with the international practice, procedures for MPs quality assessing should be validated, i.e. validation parameters should be defined, a set of which depends on the purpose of the procedure and includes the following parameters: specificity, linearity, range, limit of detection or limit of quantitation, accuracy, precision, and robustness [1, 6, 7, 16, 17].

Qualification and validation of a procedure are two different processes. Qualification of a procedure consists in the demonstration that the error of the procedure conforms to the predetermined requirements; validation consists in the assessment of the suitability of the procedure for the intended purposes. For quantitative methods the most important parameter is precision that can be assessed by standard deviation of results obtained in conditions of repeatability and intermediate precision in the whole range of procedure; this standard deviation defines the

uncertainty of the procedure [10]. The standard deviation can be higher than 20 % for biological methods of quality evaluation of biological MPs. There is no unified algorithm of validation of these procedures, therefore general recommendations in line with the State Pharmacopoeia and aspects of the procedure and its object should be considered. In view of this, RMs are very important as they provide an objective possibility to compare results of different laboratories.

Although a special regulatory basis should be elaborated, the development of RMs of medicinal products should generally include the same steps that are set out in the regulatory methodological documentation for State Reference Materials:

- elaboration of the scope of work for new RMs, elaboration of the certification programme for new batches of RMs;
- experimental preparation and certification of RMs, experimental study and monitoring of stability of RS;
- reporting on the development/certification of RMs, including all primary data; elaboration of all technical and/or supporting documentation (a certificate, layout of labels, and information leaflet);
- expert evaluation of materials on development and certification of RMs;
- approval and registration of RMs.

At present a new certificate structure for biological RMs has been developed that is consistent with the most recent international and national requirements. This structure includes all elements recommended in the relevant international documents, and also the majority of elements that are recognized in the Russian system of State Reference Materials (excluding activities related to the term “state reference material of the approved type (GSO)”). The method of determination of metrological characteristics of RMs is also excluded, because their assessment requires specifically elaborated approaches based on special aspects of a particular biological medicinal product [15].

The Eurasian Economic Union has elaborated several regulatory acts, including those governing validation of procedures for MPs, that serve as a basis for further development of national requirements in this field [16].

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THE RISK-BASED APPROACH IN THE PRODUCTION OF REFERENCE MATERIALS

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Keywords: quality management system, reference material, certified reference material, risk, risk analysis, risk-oriented approach, risk level, reference material production

Modern requirements for the reference materials production [1, 2] are based on a risk-oriented approach and planning and carrying “actions to address risks and opportunities; integrate and implement the actions into its management system processes; evaluate the effectiveness of these actions”. Formation of a management system based on risk assessment is a process of in-depth analysis and description of procedures for reference materials production, personnel and processes management, based on existing requirements and possible risks. Risk management are described by some documents [3-24] in the Russian Federation. Standard GOST R ISO / IEC 31010 [6] includes 31 methods for assessing risks that can be applied in various processes. The existing variety may be difficult for choice in the absence of some methodological recommendations for identification risk, risk analysis in the field of reference materials production. Taking into account the provisions of [5-24] this publication describes one of the possible approaches to solving this problem by the reference materials producer.

To form risk management procedure reference materials producers should form documented procedure describing:

- goals and objectives of risk management;
- documents that form on the basis of the quality management system and risks assessment;
- responsible for risk management, including specialists for identification and risk analysis, control effectiveness of eliminating or reducing the impact of risks, risk holders;
- sources of information on potential risks;
- procedure for identifying risks and their causes, assessing the probability and level of risk;
- risk management procedure taking into account their level;
- procedure for analyzing the effectiveness of risk management;
- forms of records on risk management and those responsible for maintaining records.

The analysis, identification of risks and the formulation of measures to eliminate them is the direct task of the head of the organization, carried out in conjunction with responsible specialists - department heads and a quality manager.

It is important to identify the main most significant risks that may arise from the risks arising at different stages of reference materials production. Such risks include:

- release of (C)RM with inappropriate metrological characteristics;
- release of (C)RM which material does not meet the established requirements;
- discrepancy of the period of validity of the (C)RM;
- incompleteness or inappropriate of the information in reference material certificate;
- counterfeiting of (C)RM by other legal entities.

Indicators of risks can be the results of internal, external audits, final technical products control, consumer information, etc. Important to take into account the risks relating to each process described in the relevant sections, sub-sections of the production quality manual of reference materials, documented procedures according to ISO 17034 [1]. Identification and description of risks

at each stage of the management system is the key to the thoughtful provisions in the quality manual, describing not only the rules and procedures, but also the mechanisms for effective elimination of risks at certain stages, the causes of risks.

The simplest form record of risk identification can be a passport (register) of risks, including such provisions as the name stage of the production process of reference materials, the name of the risk(s), the cause(s) of risk, document(s) (section(s)) of the management system, aimed at eliminating the risk, the probability of occurrence of risk, the level of risk, the risk holder.

Demonstration of risk management at the enterprise can be the formation of a document (for example, report), based on knowledge of risks and activities planned and conducted (conducted) in the current year by risk holders to reduce the likelihood of events associated with risks. The document can be based on the provisions of the quality manual for the reference materials production, documented procedures, quality control program (if any), a journal of preventive actions, including additional measures planned for the implementation of the current year to eliminate or reduce the likelihood of risks. The document may include such sections as: name of the risk; action aimed at eliminating the risk; period of implementation of the action aimed at eliminating the risk; responsible for eliminating the risk; information about the event, aimed at the elimination of risk; the mark of a reviewer to check the implementation of activities aimed at the elimination of risk, supporting (not proving) their effectiveness, note (e.g. information on assignments, relying formulated on the basis of tests).

The risk-oriented approach of the quality management system of reference materials production should be defined by producers as a constant, continuous, cyclic process, providing both additions and updates to the provisions of the documents of the management system related to the analysis, identification of risks and measures to address them. The basis for the updates are:

- new risks identified within the framework of the manufacturer's activities;
- experience of interaction with legal entities providing various services;
- experience of interaction (feedback) with consumers of reference materials;
- analysis of the provisions of the new documents on standardization, legal acts in the field reference materials, ensuring the uniformity of measurements, accreditation in the national accreditation system;
- improved processes for the production of reference materials.

The risk-oriented approach to the reference materials production is an effective and important unit of the producer's management system, which can become one of the basic topics for discussion among reference materials producers, in Russian Federation - among participants of the State service of reference materials (including in the light of the tasks formulated by the order of the Government of the Russian Federation until 2025 [25]).

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METROLOGICAL ASSURANCE OF INFRARED ANALYSERS OF GRAIN

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Keywords: grain, indicator of grain quality, infrared analyser, reference material

The process of grain production requires measurements of different parameters characterizing consumer properties and safety of grain. The measurements are necessary to ensure high level of quality. For example, the main indicators of grain quality are mass fraction of moisture (humidity), mass fraction of protein, mass fraction of crude gluten, mass fraction of ashes, etc. [1].

Requirements for these indicators are given in standards and product specifications. Measurements of quality indicators are carried out according to the standardized measurement procedures given in the list of the standards necessary for application and execution of requirements of Customs Union Technical Regulation “On Grains Safety” TR CU 015/2011 [2].

Application of the standardized procedures for operational quality monitoring is difficult because of high labor input and duration of analysis. Therefore, rapid test methods have been successfully applied in practice. One of the most widespread method is method of spectroscopy in near infrared area (infrared spectroscopy). The method of infrared spectroscopy is based on measurement of intensity of the infrared radiation absorbed by or diffusely-reflected from the measured sample, calculation of spectral coefficients and then calculation of mass fraction of components [3].

The main advantages of infrared analysers are high speed and accuracy of the analysis, a possibility of use without expensive reagents and also a possibility of simultaneous definition of several indicators (protein, moisture, gluten, etc.).

For many years for assessment of metrological characteristics of analysers (when carrying out type approval tests and verification) special grain samples (prepared and certified in accordance with GOST R 8.593-2002 [4], with certified values determined by the standardized procedures) were used.

However, nowadays according to Federal Law of The Russian Federation No. 102-FZ “On ensuring the uniformity of measurements” [5], it is necessary to use certified reference materials for verification and type approval procedures. Reference materials are the most effective means of metrological assurance for expensive and large-size infrared analyzers, because they provide an opportunity for carrying out on-site verification.

Consequently, scientific metrological institute had a task to develop a set of reference materials, which was necessary for carrying out verification in the state regional centers of standardization, metrology and tests.

So, laboratory of metrology of moisture content measurements and reference materials has developed a set of reference materials for metrological assurance of measurements of main quality indicators of grain. The list of the developed reference materials (further RMs) is given in table 1.

T a b l e 1. List of certified reference materials released by laboratory of metrology of moisture content measurements and reference materials

Registration number and name of RM	Measured characteristic	Range of certified values, %	Limits of acceptable values of absolute error when P = 0,95
GSO 8990-2008 2nd category reference materials of mass fraction of moisture of grain	mass fraction of moisture	7,0 – 25,0	± 0,2 %
GSO 9734-2010 Reference materials of composition of grain and products of grain processing	mass fraction of protein	5,0 – 50,0	±0,25 % in the range from 5,0 % to 16,0 %; ±0,30 % in the range from 16,0 % to 31,0 %; ±0,35 % in the range from 31,0 % to 50,0 %
	mass fraction of moisture	7,0 – 25,0	±0,2 % in the range from 7,0 % to 18,0 %; ±0,3 % in the range from 18,0 % to 25,0 %
GSO 10887-2017 Reference materials of mass fraction of crude gluten in grain	mass fraction of crude gluten	19,0 – 35,0	± 0,6 %

RMs have the same matrix as measured material and are made of specially prepared high-quality and ordinary grain and leguminous crops. The certified values of mass fraction of moisture and protein are determined with application of the standards applied in UNIIM. The certified value of mass fraction of crude gluten is determined on the basis of interlaboratory experiment.

It should be mentioned that all RMs are recognized as the interstate reference materials and have been entered into the register that allows to apply them without restrictions in the countries which have joined recognition (Table 2).

T a b l e 2. List of RMs recognized as interstate RMs

Registration number of interstate RM	Name	Recognized by
MSO 1790:12	2nd category reference materials of mass fraction of moisture of grain	Azerbaijan, Armenia, Belarus, Kazakhstan, Kirghyzian Republic, Moldova, Tajikistan, Turkmenistan, Uzbekistan, Ukraine
MSO 1782:2012	Reference materials of composition of grain and products of grain processing	Azerbaijan, Armenia, Belarus, Kazakhstan, Kirghyzian Republic, Moldova, Tajikistan, Turkmenistan, Uzbekistan, Ukraine
MSO 2113:2017	Reference materials of mass fraction of crude gluten in grain	Armenia, Belarus, Kazakhstan, Kirghyzian Republic, Tajikistan, Turkmenistan, Uzbekistan, Ukraine

Nowadays, not only regional centers of standardization, metrology and tests are interested in buying RMs, but also organizations, which are carrying out measurements of grain quality indicators by the standardized procedures, for the purpose of control of measurement accuracy.

Now, UNIIM is working on development of a set of reference materials of mass fraction of ashes, calcium, phosphorus.

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EXTERNAL CONTROL OF THE QUALITY OF FOOD COMPOSITION MEASUREMENTS USING INTERLABORATORY COMPARISON SAMPLES

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Keywords: quality control of food products, laboratory proficiency testing, interlaboratory comparisons, reference material, proficiency testing samples, ILC sample, ILC provider, quality assessment of test results

This paper is devoted to issues associated with the assessment of the quality of information on the composition and properties of food products. As a rule, food producers declare the quality of their production on the basis of measurements carried out in laboratories determining food composition and properties. However, it is no secret that some products on shop shelves still fail to meet rigorous quality requirements. The most important factor in preventing such situations is the external quality control of laboratories testing (analysing) food production.

Testing laboratories are supposed to regularly confirm the correctness of their conclusions about the composition and properties of products under analysis. According to the policy of the RF Federal Accreditation Service (Rosaccreditation), an accredited laboratory is to take part in interlaboratory comparison (ILC) studies in order to verify all the test methods added to the scope of its accreditation within 5 years from the date of the accreditation decision. Accredited ILC providers assess the quality of measurements carried out by testing laboratories.

During the proficiency testing of laboratories (quality assessment of their measurements), proficiency testing samples (ILC samples) are used, which can be either certified reference materials, test portions, product samples or their imitations. ILC providers pay special attention to the samples used for ILCs, their homogeneity and stability.

It is shown that real samples taken from the same batch of food products, produced by the same manufacturer and meeting all quality requirements may differ in their composition (properties) due to heterogeneity and instability problems arising during the shelf life and storage conditions.

The possible types of proficiency testing samples and the examples of their creation are provided. Approaches to establishing the assigned values of samples (those values, with which the results of measurements conducted in various laboratories are compared) are described. The specimens of proficiency testing samples are sent to laboratories for ILC. An algorithm for obtaining conclusions about the quality of measuring an ILC sample in a laboratory is presented. When processing the data, the ILC provider takes into account the uncertainty of measurement acceptable for testing laboratories. Approaches to establishing values of acceptable measurement uncertainty are described. Specific examples of ILC implementation in food industry are given.

This paper concludes that participation of testing laboratories in ILC studies on a regular basis allows the quality of food products to be sustainably confirmed, thus ensuring consumer confidence in their composition and properties.

EVALUATING LONG-TERM CAPABILITY IN PRIMARY pH METROLOGY USING TECHNIQUES OF THE CCQM KEY COMPARISONS IN pH

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CCQM Key Comparisons in pH (KC) assess the primary pH measurement capability of participants by evaluating the Degrees of Equivalence (DoE), the difference between the results of a given participant and a measure of central tendency of all results, the Reference Value (RV). The uncertainty of the DoE gives a quantitative estimate of a participant's measurement capability for a single buffer at a single point in time.

The long-term performance of a given participant may be assessed using an analogous approach with multiple measurements (i.e., batches) of a pH reference material (RM) over time, i.e., a longitudinal meta-analysis. Here, the RV is the mean (over all batches) at each temperature, T. The analog to the DoE, $\Delta pH(S)$, is the difference between the reported value for a given batch and the RV. The standard deviation of $\Delta pH(S)$ yields a quantitative estimate of the performance of this participant at each point in time. Batch-to-batch differences in the RM composition (buffer ratio) yield T-independent (constant) deviations in $\Delta pH(S)$ and do not contribute to the standard deviation of $\Delta pH(S)$. In contrast, T-dependent changes in $\Delta pH(S)$ result from artifacts of the measurement process.

Examples are shown using data taken from pH RM certified by the National Institute of Standards and Technology (NIST), USA, over a period of 70 years.

FALSIFICATION OF CERTIFIED REFERENCE MATERIALS. HOW TO IDENTIFY AND HOW TO FIGHT?

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Keywords: reference materials (RMs), ensuring the uniformity of measurements, RM distribution, quality control, RM identification, falsification, evaluation of RM suitability, RM labels.

According to legal [1] and normative documents [2] reference materials (RMs) are intended for:

- reproduction, storage and transfer of the characteristics of the composition or properties of substances (materials);
- demonstration of calibration and measurement capabilities;
- check of the testing laboratories competence during accreditation;
- interlaboratory comparison for validation of non-standardized measurement procedure and proficiency testing.

Because of such responsible field of applications requirements for RMs are very high.

One of the key factors that ensure the quality of measurements is the suitability of RMs with property values that can be relied upon by their users.

The producers of RMs spend a lot of effort: characterization by metrological reasonable procedures, traceability to the national primary standards, clear RM identification and more. However, this brings results only with competent distribution and application. In particular, user shall read the accompanying documentation of RMs, and for this passport (certificate) should be clearly correlated with the RM unit.

Not so long ago, we, as RM producer, faced a new problem – falsification.

Our customers helped us to identify this problem. Fortunately, consumers of RMs are vigilant and active participants of the system for ensure the uniformity of measurements. This is clear, the responsibility of the laboratory for the quality of the used RMs even established by the requirements of ISO/IEC 17025 [3]: the laboratory shall have access to equipment (including, … reference materials, …) that is required for the correct performance of laboratory activities and that can influence the results.

A demonstrative example of falsification is shown in Fig. 1. The label on the box is different from the original very much, what is more, it has the gross errors: the abbreviation GSO is absent, “formazine suspension” is written incorrectly, the batch indication contains the excess “C”.

We give a lot of attention to labeling. We not only meet the established requirements for the content [4 – 6], but also strive to provide high quality of labels, which are difficult to copy in the artisanal conditions. Regular customers are already accustomed to our traditional design of labels and packaging boxes. If they receive RMs with a label of inadequate quality or in non-original packing, it is an occasion to address us to confirm originality of RMs.

Because of such messages were identified some cases of falsification of our products.

“Our laboratory gat RM of turbidity, as indicated, manufactured by “CRM” I want to know whether this RM is produced your company, as the appearance of packing and ampoule's labels is questionable. Photo is attached.”

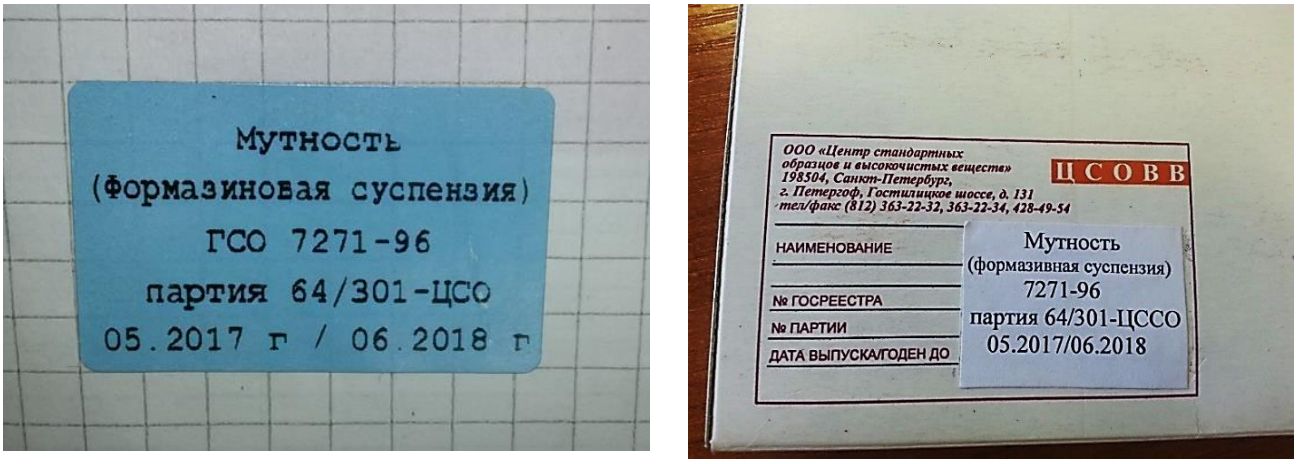

Fig. 1. Label for the packaging box for RM of turbidity (formazine suspension): left - a control sample of the original label, right - a falsified label pasted on the original box (when making a label made a number of gross errors)

Another example.

“According to the orders RMs from the producer of “CRM” was purchased. The package included a copy of the passport without the blue stamp. The following inconsistencies were noted in comparison with the previous batch: producer's label on the package, batch number and date of manufacture are absents (photo is attached).”

For identifying fakes it also help public issuance information about RMs, which are in circulation. This requirement for competent RM producer is very useful in practice. Following our recommendations the users are already accustomed to watch this information. Therefore, as soon as they find difference between information on our website and data of RM's certificate they immediately ask us to explain.

It should be noted that until now there have been no erroneous appeals. Every questionable case turned out to be a fake!

We had to deal with informational falsification, that is, false information about the product was presented. The revealed facts of falsification were the change of the original labels and recording false information in the RM certificate. As far as we were able to understand, this was done by intermediaries to sale RM, which have the shelf life already expired.

How to fight? In this matter our weapons – competence and observation!

For each case we analyze whether there is a falsification, where and how it was possible. Intermediaries-suppliers are attracted to this investigation. Herewith they behave variously: some admit mistakes and strive to correct them, others do not give any comments. Our organization includes the latter in the so-called “black list”, as working with unscrupulous distributors can have serious negative consequences.

After all, it should be reminded these actions fall under the scope of articles of the Civil Code of the Russian Federation on the delivery of goods of improper quality and the Criminal Code on the manufacture and use of a knowingly forged document.

However, because of the use of falsified RM laboratory may suffer damage that is higher than the cost of this product. The ability of the laboratory to obtain reliable test results is compromised. When an unscrupulous supplier changes the production date and the batch numbers, he breaks the connection the unit of RM with the certificate, where the certified value is specified. Thus, even if the shelf life has not yet expired, the user can no trust the specified values of the characteristics.

It is possible that cases of falsification have occurred before, but information about this began to come to us only in 2015. We suppose that this is due to the increase of requirements for accompanying documentation of RMs and competence of users.

Producers of RMs themselves should be interested that users study carefully the accompanying documentation of RMs, could establish the authenticity of RMs by its characteristic features (for example, a typical package), may obtain advice from the producer.

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THE USE OF A REFERENCE MATERIAL TO SOLVE PROBLEMS IN ASSESSING THE QUALITY OF ELECTRICAL STEEL IN ACCORDANCE WITH THE REQUIREMENTS OF RUSSIAN AND FOREIGN STANDARDS

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Keywords: standard, measurement standard, reference material, magnetically soft material, electrical steel, magnetic loss, measurement method

In connection with the growth in the volume of international trade relations in the field of supply of electrical steel, the issue of timely alignment of requirements of regulatory documents about quality of the materials produced is quite acute. The development of new approaches in industry, allowing optimizing the properties of electrical steel, also necessitates the updating of normative documents for the materials and methods for control of their properties. For electrical steel, the main characteristics that determine its suitability for various applications are dynamic magnetic properties (in particular, the specific power of magnetic losses). There are a number of differences between the methods of measuring these characteristics, described in the standards of the Russian Federation and foreign countries. These differences concern both the design features of the equipment used and the algorithms for obtaining the values of the measured quantities.

The aim of the study was to identify major discrepancies and search for possible solutions to the existing problems. For this, the regulatory documentation ordering the requirements for the materials and methods for control of their properties in Russia and abroad was studied. Measurements of the magnetic characteristics of electrical steel were performed via magnetic measuring devices used in accordance with the requirements of Russian standards GOST 12119.4 [1], GOST 12119.5 [2] and IEC 60404-3 [3]. For the measurements cold-rolled grain-oriented electrical steel of different thicknesses and with different properties including steel with an optimized domain structure (laser treatment of the surface of rolled steel) was used. The measurements were carried out using device that is part of the state primary standard GET 198-2017 [4], via magnetic measuring device of the PTB (Germany) and the MPG 100 D. When choosing the parameters for performing measurements, the requirements of the standards defining the rules for their use were taken into account and the differences found between them.

From the analysis of the results obtained, it was concluded that the use of various measurement parameters established in accordance with the requirements of the standards could lead to a significant difference in measurement results. In this, the conditions were determined for which the results of measurements obtained using the magnetic measuring device of the PTB and the device from the GET 198-2017 coincide within the frames of measurement capabilities of these systems. The results of the research show the need to work on the uniformity of the requirements of standards in the field of assessing the quality of electrical steel which are used in Russia and abroad. The practical significance of the results obtained lies in the definition of the key differences between the measurement techniques used and the detection of parameters that have the most influence on the final measurement results.

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A NEW MULTIELEMENT REFERENCE MATERIAL FOR COMPOSITION OF PINE NEEDLES

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Keywords: plants, pine needles, elemental analysis of chemical composition, interlaboratory comparison, certified value, multielemental reference material (RM)

Plants bind together the atmosphere, biosphere and hydrosphere, affecting the climate and changing under its influence. The plants receive different trace elements from the soil pore water, and the content of these trace elements usually correlated with the geochemical background of the region of plant growth. Trace elements are more intensive transferred and excess accumulated in biota in areas with a high their content. Therefore, some types of plants are used as biogeochemical indicators for exploring ore deposits [1] and for assessing the degree of environmental pollution as a result of anthropogenic impact [2]. The existing reliable and comparable to each other the results of chemical analysis needed to study biogeochemical processes [2-4] are not enough. One way to ensure the reliability of analytical data is to use reference materials (RMs) of biota composition for the calibration of analytical techniques and accuracy control of the results. Despite the species diversity of plants, in the State Register of the Russian Federation the list of multielement RMs from them is very modest [5]. Therefore a new multielement RM of pine needles HSS-1 (Pinus Sylvestris) was developed in addition to the three CRMs of plants previously created in the IGC SB RAS [6]. Pine grows in a humid and arid climate and is a sensitive indicator of environmental pollution. The high content of physiologically active substances in the pine tree determines its great value as raw materials for obtaining various pharmaceutical preparations and feed products.

Pine needles were collected in the summer near the lake Baikal, and then the material was dried, crushed and homogenized. Granulometric composition, homogeneity and stability of this material were investigated. In 2015-2016, interlaboratory certification experiment was planned and carried out in according to the requirements of ISO Guide 35 [7]. The certified reference materials – Canadian pondweed (EK-1), Mixture of meadow herbs (Tr-1) and Birch leaf (LB-1) [6] – after studying their stability in the conditions of natural aging [8] were used for evaluating traceability. More than 1,800 measurements of 12 analytical methods from 20 laboratories were processed. The contents and their errors of 28 elements are certified, for 12 elements content values are recommended. The comparison of pine needles and three CRMs of plants (LB-1, Tr-1, and EK-1) showed their consistency and the possibility of simultaneous use. The new multielement RM HSS-1 (*Pinus Sylvestris*) is made to certify measurement techniques applied in determining the composition of plant origin objects; accuracy control (precision and trueness) of the results of chemical, physical and physicochemical methods of laboratory analysis, as well as professional testing of laboratories of geological, agricultural and pharmaceutical organizations.

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DEVELOPMENT OF A CERTIFIED REFERENCE MATERIAL OF 0.1 M POTASSIUM DICHROMATE SOLUTION GSO 10992-2017

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Keywords: coulometry, coulometric titration, titrimetry, GET 176, potassium dichromate solution, certified reference material, certified value uncertainty

Potassium dichromate is a common standard substance in titrimetry which is widely used in world laboratory practice as a titrant for the determination of most reductants, due to its high stability in water solutions and oxidizing properties [1]. If there is a task to achieve the high accuracy and ensure metrological traceability, titrants based on potassium dichromate are prepared from a certified reference material (CRM) of potassium dichromate, for example GSO 2215-81. The CRM GSO 2215-81 was certified by the primary method [2] of coulometric titration using State Primary Standard of the mass (molar) fraction and mass (molar) concentration of components in liquid and solid substances and materials based on coulometry GET 176 [3]. The trueness of the measurement results of the main component mass fraction in potassium dichromate obtained by using GET 176 has been confirmed by bilateral [4] and key [5] international comparisons. The database of measuring and calibration capabilities of the International Bureau of Weights and Measures (BIPM) includes a corresponding line (CMC) [6]. Further stages of transferring a unit of the main component content from GSO 2215-81 to CRMs, RMs, chemical reagents and their solutions contain a number of factors that can influence on the trueness of measurement results when the laboratory lacks the necessary skills or experience. These factors are drying the solids to the constant weight, preparing titrants of the definite concentration, calibrating the measuring laboratory glassware, etc., In order to exclude or minimize the negative impact of these factors, especialy during measurement results accuracy control, for laboratories it is convenient to use a ready-made titrant solution. The developed CRM of the 0,1M potassium dichromate solution is the second one in the line of high-precision CRMs of the high purity substances’ solutions produced by UNIIM using GET 176.

CRM Description

The certified reference material is a 0,1M solution of a recrystallized chemical reagent of potassium dichromate (produced according to the requirements of GOST 4220-75 “Reagents. Potassium bichromate. Specifications”) in deionized water with conductivity less than $1 \cdot 10^{-5}$ S/m. The certified value is the molar concentration of potassium dichromate in the range from 0.098 to 0.102 mol/dm^3.

The CRM is packed into 250 cm^3 plastic bottles with a screw caps, additionally insulated by paraffin or heat shrink tubing. The appearance of the CRM unit is shown in Fig. 1.

Evaluation of the CRM uncertainty from instability

In modern practice of production of CRMs of substances and materials, according to ISO Guide 35 [7], two characteristics of CRM instability (short-term and long-term instability) are to be investigated. For the CRM of the high purity substances’ solutions both these characteristics are arisen from the various factors such as chemical and physical processes in solution (for example, adsorption), leakproofness of packaging, permeability characteristics of the bottle material, exposure to potentially influencing factors such as temperature, ultraviolet, and others. It seems to be too complicated to evaluate the effects of all the influencing factors separately, therefore, an assessment

of the CRM stability is carried out empirically for each CRM and for each type of packaging used. The value of the standard uncertainty from instability in this case is expressed as the standard deviation of the coefficient of linear dependence of the measurement result from the time and through the shelf life of the CRM.

Fig. 1 . The appearance of the CRM unit of 0,1 M potassium dichromate solution

The long-term stability of the CRM of the potassium dichromate solution was estimated by the accelerated ageing method according to the algorithm given in the document P 50.2.058-2007 “Recommendations on metrology. State system for ensuring the uniformity of measurements. CRMs’ certified values uncertainty evaluation”. The ageing temperature was set at (60±2) °C taking into account that the maximum melting point of the insulating paraffin is 65 °C (GOST 23683-89 “Petroleum paraffin waxes. Specifications”). The standard uncertainty from instability for 1 year storing is 0.004 %.

The short-term stability of the CRM of the 0.1 M potassium dichromate solution was investigated during the study of long-term stability. The critical temperature conditions permissible during transportation of the CRM correspond to the maximum preservation temperature of the package (60 °C). Studies of stability under critical conditions were carried out for 11 days. The standard uncertainty from short-term instability of the CRM is assumed to be numerically equal to the standard uncertainty from the long-term instability of the CRM.

Determination of the CRM certified value

The CRM certified value was established by direct measurements of the molar concentration of potassium dichromate by the method of coulometric titration using one of the installations included into the State primary standard of units of mass (molar) fraction and the mass (molar) concentration of components in liquid and solid substances and materials based on coulometry, GET 176-2017.

The estimation of uncertainty characteristics was carried out in accordance with the requirements of GUM [8]. The certified value was calculated as an arithmetic mean of nine measurements of the molar concentration of potassium dichromate. The type A standard uncertainty was estimated as the standard deviation of the mean of all measurement results. The type B standard

uncertainty was evaluated as a composition of standard uncertainties from the measuring instruments used, reference data [9] and [10] and from the influencing chemical factors (oxygen effect, diffusion of the determined component into the cell's auxiliary chamber, presence of electroactive impurities in the electrolyte, etc.)

The limits of the relative error were estimated by the algorithm given in GOST 8.736-2011 “State system for ensuring the uniformity of measurements. Multiple direct measurements. Methods of measurement results processing. Main principles”, taking into account the characteristics of short-term and long-term CRM stability.

The metrological characteristics of CRM are given in the Table 1.

T a b l e 1 – The metrological characteristics of CRM of 0.1 M potassium dichromate solution

Certified characteristic	Certified value, mol/dm^3	Relative expanded uncertainty of the certified value (k = 2), %	Limits of the relative error of the certified value (P = 0,95), %
Molar concentration of potassium dichromate	0,100509	0,024	±0,026

Conclusion

As a result of research, the certified reference material of 0.1 M potassium dichromate solution (0.1 M $K_2Cr_2O_7$ CRM UNIIM) was developed, manufactured and tested. CRM has been given a number in the State Register of approved types of CRM as GSO 10992-2017 [11]. The CRM is intended for transferring the unit of the mass (molar) concentration of the component to CRM, RM and chemical reagents by the oxidation-reduction reactions; calibration of measuring instruments, metrological characteristics control during measuring instruments testing, including for type approval purposes; attestation of measurement procedure, accuracy control of the measurement results for the mass (molar) fraction and mass (molar) concentration of components in liquid and solid substances and materials.

The developed CRM of the 0.1 M potassium dichromate solution is a ready and convenient tool for laboratories to monitor both the procedure for preparing the titrant and the final result of measurements of the component content in the substance being analyzed. And also the CRM GSO 10992-2017 using will significantly reduce the preparation time for measurements.

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WORK ON THE PRODUCTION OF CERTIFIED REFERENCE MATERIALS, PERFORMED BY WESTERN-SIBERIAN TESTING CENTER IN 2017-2018

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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, 13 reference materials of West-Siberian Testing Center have the status of approved type, 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, the interest of consumers to reference materials production of West-Siberian Testing Center has significantly increased. The marketing policy of the organization contributes to the increase in sales volume, as well as the growth in consumer demand was provided by an increase in the number of regional testing laboratories specializing in analyzing coal samples. Consumers demanded from all ranks of coal, as the reference materials are certified for different intervals of indicators and, thus, allow to solve different analytical problems.

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

- 2017 – developed and approved by GSO 10893-2017, GSO 10894-2017, GSO 10895-2017, GSO 10896-2017, reference materials of coal rank GZhO, OS, G, T;
- 2018 – developed and approved GSO, reference material of the composition of polymetallic ore of the Quartz Sopka field. The validity period of GSO 7460-98, reference material of ash of hard coal composition was expended, and the area of its application was expanded.

At the moment West-Siberian Testing Center is developing two state reference materials of coal (rank fat, jetcoal). The certification is carried out by the method of interlaboratory experiment, in which 28 laboratories of Russia and the near abroad participate.

In 2019, it is planned to produse two reference materials of rank jetcoal, lean coal with a high content of sulfur content in total (0,7-1,0 %).

In the testing laboratory of 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.

Information on the GSO for composition of rocks, ores, coal, ash and slag wastes, developed by 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

No.	Description	Parameter	Duration of use
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 8515-2004 Iron ore (RM-20)	Fe_2O_3, FeO, SiO_2, TiO_2, Al_2O_3, MgO, MnO, CaO, Na_2O, K_2O, P_2O_5, S_{total}, Cu, Pb, Zn	until 2023
9	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
10	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
11	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
12	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
13	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

PROFICIENCY TESTING WITH THE ESTABLISHED TRACEABILITY TO THE NATIONAL PRIMARY STANDARD GET 176-2017

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Keywords: inter-laboratory comparison, proficiency testing, traceability, coulometry, direct primary method, pure substance, copper sulfate, hydrochloric acid, potassium hydrogen phthalate, potassium dichromate, potassium chloride

Interlaboratory comparison (proficiency testing - PT) is an effective tool for checking the quality of measurements in the testing laboratory, as well as for the assessment of the staff qualification. In recent years, the interest of testing laboratories to participation in the PT has been growing steadily. A legally fixed requirement for the testing laboratories to take part in the PT (Order of the Ministry of Economic Development № 326 of 30.05.2014 “On approval of accreditation criteria... ”) has played a certain role in this process. At the same time the number of PT providers, both accredited and non-accredited, is increasing. Nevertheless the list of PT objects is not so wide. Traditionally, the most popular objects are water of different categories, soil, oil products, some types of food products.

For a testing laboratory willing to meet the legislation requirements and provide the results of participation in the PT schemes it can be difficult to choose a competent provider. Generally, when choosing a provider it is useful to consider the following factors:

- Provider measuring equipment availability to self-control the values of the determined characteristics in the round;
- the established traceability of the assigned values for all determined characteristics;
- the recognized quality management system;
- an experience in working with similar objects and measurement results treatment obtained in PT.

UNIIM is an accredited PT provider and a holder of 10 state primary standards and more than 200 working standards. The laboratory 223 is the developer and holder of the State primary standard of mass (molar) fraction and mass (molar) concentration of the components in liquid and solid substances and materials based on coulometry GET 176-2017 [1, 2]. At the moment, GET 176-2017 includes 3 reference installations implementing two types of direct primary measurement method of coulometry (controlled-potential coulometry and coulometric titration) and mass spectrometry with inductively coupled plasma. Each of reference installations has participated in international comparisons of different levels - bilateral cooperation, the comparisons in the framework of the Euro-Asian regional Metrology organization COOMET, pilot studies carried out by the Consultative committee of Amount of Substance of the International Bureau of Weights and Measures (BIPM) and in comparisons of the highest level - the BIPM key comparison (a total amount is more than 15 comparisons since 2004 [3-6]). GET 176-2017 successful participation in the international key comparisons in the frame of BIPM has resulted into seven lines of the calibration and measurement capabilities (CMCs) in the field of the main component content measurement in high purity substances.

Since 2016, laboratory 223 has started organizing rounds of PT for objects and characteristics, the accuracy of measurements of which was previously confirmed at the highest metrological level by participating in international comparisons. In these rounds the assigned values

determination was carried out using the State Primary Standard GET 176 being confirmed its equivalence to the national standards of the world leading countries. Table 1 shows a matching of the organized rounds of the PT schemes and the relevant international comparisons.

T a b l e 1. List of the organized rounds of the PT schemes with implemented traceability to the State Primary Standard GET 176-2017

PTs with implemented traceability to GET 176		**International comparisons involving GET 176**			
Code number and a name of PT round	Analyte	Code number and a name of the international comparison (IC)	Analyte	Assessment of UNIIM participation in the IC	CMC presence in the BIPM database for 15.07. 2018
MSI 223-SM-1/2016 “Determination of the composition characteristics of the blue vitriol”, MSI 223-RSM-1/2017 “Determination of the composition characteristics of the copper (II) sulphate pentahydrate”	Cu^{2+}	**COOMET 645/RU/2014** “Pilot comparison in the field of measurements of the mass fraction of coper and impurities in the oxygen-free copper wire rod of the brand KMB M001b for coper purity determination” **CCQM-K143 (2017-2019)** “Comparison of Copper Calibration Solutions Prepared by National metrological institutes/designated institutes”	Cu^{2+}	+ Comparison is not completed, the preliminary result is positive	No
MSI 223-KS-1/2017 “Determination of the composition characteristics of the hydrochloric acid”, MSI 223-KS-2/2018 “Determination of the composition characteristics of the hydrochloric acid”, MSI 223-BFT-1/2017 “Determination of the composition characteristics of the potassium hydrogen phthalate”	H^{+}	**CCQM-P19.2 (2008 -2012 гг.) “Assay of H^{+} in hydrochloric acid”** **CCQM-K34.2 (2008-2009 г.)** “Assay of potassium hydrogen phthalate” **CCQM-K34.2016 (2016-2017)** “Assay of potassium hydrogen phthalate”	H^{+}	+ + +	Yes [7]
MSI 223-BHR-1/2017 “Determination of the composition characteristics of the potassium dichromate”	$Cr_2O_7^{2-}$	**CCQM-K96 (2011-2013)** “Assay of potassium dichromate”	$Cr_2O_7^{2-}$	+	Yes [7]
MSI 223-SP-1/2018 “Determination of the composition characteristics of the sodium chloride (table food salt)”	Cl^{-}	**CCQM-K48.2014 (2014-2016)** “Assay of potassium chloride”	Cl^{-}	+	Yes [7]

Proficiency testing schemes with implemented traceability to the State primary standard, the measuring capabilities of which were confirmed by successful participation in international key comparisons and were fixed as CMCs in the database of the International Bureau of Weights and Measures, is a logically completed chain of transfer of metrological service from the top level (State primary standard) to the consumer, i.e. testing laboratory. In this case, the testing laboratory can be sure in getting metrological services of assessment its competence on the basis of high-precision and

traceable measurement results from a truly competent provider, whose qualification has been confirmed at the international level.

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DEVELOPMENT OF REFERENCE MATERIALS FOR POROSITY BASED ON ALUMINUM OXIDE FOR THE METHOD OF MERCURY POROSIMETRY

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Keywords: mercury porosimetry, reference material, metrological traceability

Creation of new porous materials, the quality of which must be controlled, dictates the introduction of a wide range of instruments for measuring porosity characteristics. In particular, the pore size significantly affects the performance of ceramic filter elements, which are intended for separating, concentrating and purifying various liquid mixtures from dispersed components, as well as for separating gas mixtures and purifying them from various dispersions. One of the most highly accurate methods for measuring pore size within the range from 100 nm to 0.9 mm is the mercury porosimetry method. It is distinguished by its great versatility, since it makes it possible to obtain information about the porous structure in a wide range of pore sizes, and its design equations are distinguished by simplicity [1-3]. It is also possible to use this method for measuring the specific surface area of dispersed bodies under conditions when powder has a relatively low surface energy and mercury does not wet the surface of its particles, when there are no one-side open pores and the pressure in the porosimeter allows penetration of mercury into the smallest micropores of the material [3]. The objects of application of mercury porosimetry are rocks and ores, pigments, carbon and graphite, catalysts and minerals, glass, coatings, adsorbents, fertilizers, coal, filters, fillers, fabrics and fibers, gaskets, fibrous plates, refractories, paper, nuclear fuel, metal slags and composite materials. Mercury porosimeters determine the total pore volume and pore size distribution, total pore surface area, average pore diameter, bulk density and true density. The method of mercury porosimetry is based on the fact that mercury, which does not wet a solid, penetrates into its pores only when exposed to external pressure. However, there are currently no measuring instruments of approved type in Russia that are based on the mercury porosimetry method, as well as the corresponding reference materials of the approved type.

Therefore, this paper is devoted to the development of reference materials for porosity based on aluminum oxide for the method of mercury porosimetry. The following materials were selected as initial ones for the creation of reference materials:

- 3 different ceramic filter elements produced in line with TU 3614-001-18985634-2006 which are porous membranes based on α-phase aluminum oxide;
- granular aluminum oxide, produced in line with TU 2163-015-94262278-2009.

The pore size of these materials varies over a wide range from 12 nm to 60 000 nm.

Research of metrological characteristics of candidate reference materials are held on a reference installation, which is planned to be included into GET 210 - 2014 National primary standard of units of specific adsorption of gases, specific surface area, specific volume and pore size of solids and materials [4] at the end of 2019. It includes the following equipment: a mercury porosimeter providing a range of pore size measurements from 0.0036 μm to 900 μm; a mercury purification kit; a kit for calibrating the volume of mercury that intrudes into the material; a set of dilatometers for the measurement of compact and granular materials; a personal computer with specialized software; a laboratory balance (special accuracy class I); a gas pycnometer that can maintain a set temperature within the range from 18 to 35 °C and measure the density of solids and

materials within the range from 2 to 23 g/cm^3; a pressure calibrator with absolute pressure sensors with a limit of measurements from 400 kPa and 400 MPa, the limits of permissible reducial error of absolute pressure are ± 0 025% and ±0.1% respectively; an indicator for the determination of mercury vapor in the ambient air.

Homogeneity and stability of granular alumina material with the pore size of 12 nm has been studied earlier with the help of gas adsorption method [5], that is why the work is directed at the estimation of characterization uncertainty of the following quantities with the help of mercury porosimetry: specific pore volume, specific surface area, the predominant and average pore size; as well as pressures, which correspond to 25 %, 57.5 % and 87.5 % of the specific saturation volume.

Membranes based on α-phase aluminum oxide are a new material, that is why a full cycle of homogeneity and stability works is carried out with them. The average pore sizes of the membranes under study are ~ 1000 nm, ~ 8000 nm, 58000 nm.

Development of reference materials will provide metrological support for the porosity SI for solids and materials based on the method of mercury porosimetry in various industries. At the same time metrological independence of the Russian Federation will be ensured and import substitution of expensive foreign RMs implemented.

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DEVELOPMENT AND CERTIFICATION OF ICP STANDARD SOLUTION OF LEAD

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Keywords: inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectroscopy, water, aqueous solution, reference material, lead, water analysis, inorganic component

Control of the content of inorganic components in various materials is an extremely important problem. All branches of science and industry are interested in solving this problem. The issue of water quality control becomes more important every year because of different factors – technical progress, the rapidly developing industry, steady increase of population density in large cities.

Access to safe drinking water is essential for the health of the world's population. Monitoring of water quality and taking timely measures to improve it can prevent adverse public health consequences, which in turn will reduce health care costs. Each country has its own requirements for the quality of drinking water. It is tested for 93 indicators in Russia, for European countries the number of tested indicators varies within 50-60. A lot of national and international organizations publish recommended methods for water analysis. Chemists basically focus on many parameters to choose the method of analysis. It is very important that the method should provide the required accuracy.

A lot of analytical laboratories equipped with inductively coupled plasma optical emission spectrometers and inductively coupled plasma mass spectrometers for performing elemental inorganic analysis of various objects.

A key condition for successful implementation of the above-mentioned modern instrumental methods in laboratories is their providing by reference materials. A complex of primary national standards was developed in order to ensure the uniformity of measurements in the field of physicochemical measurements of the composition of liquid and solid substances and materials. The complex includes the National primary standard of mass fraction units and the mass (molar) concentration of inorganic components in aqueous solutions based on gravimetric and spectral methods (GET 217-2018). According to GOST R 8.735.0-2011, one of the means of metrological traceability of the value from the GET 217-2018 is reference materials.

ICP Standard solution of lead was developed in National Research Institute for Physicotechnical and Radio Engineering Measurements. Certified value metal content in the material is expressed as mass fraction, indicating the material density in the certificate. Developed ICP Standard solution with low content of impurities, suitable for calibrating inductively coupled plasma optical emission spectrometers and inductively coupled plasma mass spectrometers.

DEVELOPMENT, PRODUCTION, TESTING AND USE OF CERTIFIED REFERENCE MATERIALS FOR METALLURGICAL PRODUCTION

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Keywords: production of reference materials (RMs), interlaboratory certification of CRM, the tests of CRM for type approval, a state of metrological traceability of certified values

Since the year 1963 the Institute for Certified Reference Materials (ICRM) produced CRMs for chemical analysis in metallurgy. Over 500 individual CRMs produced by ICRM so far have been registered.

The ICRM programme covers the entire material range of the ferrous metallurgy – from raw materials (ores, ferroalloys, refractories) over technical metals to by-products and wastes (slags, flue dusts).

The CRMs are produced both in a particulate form (powder, chips, pins) for the wet-way and combustion/thermo evolution analysis and as compact samples for spectrometry.

ICRM successfully developed and produced CRMs in the last years. There were produced 67 CRMs in 2015-2018, including 34 CRMs for chemical analysis and 33 CRMs for spectrometry.

CRMs for chemical analysis:

- 18 CRMs of carbon steel, low alloy and alloy steel
- 2 – of cast iron
- 5 – of ores and concentrates
- 6 – of ferroalloys (silicomanganese, carbon ferromanganese, ferrochrome, ferrochrome nitrated, metal chromium, silicocalcium).
- 2 – of metallurgical slags.

CRMs for spectrometric methods:

- 22 CRMs of steel and
- 11 CRMs of cast iron.

ICRM is accredited in accordance with the requirements of the International Standard ISO Guide 34:2009 (ISO Guide 34)[1], the scope of accreditation includes all materials, listed above.

In 2015, ICRM was accredited in the field of providing the uniformity of measurements for works and (or) provision of services for testing CRMs for approval of the type.

The main way of method of determination the metrological characteristics of a CRM is an interlaboratory experiment – and this is an international practice of characterization CRM of metallurgical production materials, having a complicated chemical composition. Annually up to 90 analytical laboratories participate in the proficiency tests for the characterization of CRMs developed by the institute. ICRM is accredited as a the proficiency tests provider in accordance with the requirements of GOST ISO/IEC 17043: 2013. Demonstration of the metrological traceability of the values of CRMs, certified according to the results of the proficiency tests, requires additional discussion. In a sense, proficiency tests can be considered an analog of comparisons of measurement standards.

[1] The accreditation body is the AAC "Analitica" (a member Multilateral Agreement on mutual recognition of the equivalence of ILAC accreditation results).

Chemical analysis of CRM materials at all stages of production is performed by the Test Analytical Center of ICRM, accredited in accordance with GOST ISO / IEC 17025-2009. The Center applies more than 500 measurement techniques based on various analytical methods of “wet chemistry”. The results of the analysis can be traced to pure metals and compounds of stoichiometric composition. Measurements are carried out on modern analytical equipment.

The qualification of the Test Analytical Center of ICRM has been repeatedly confirmed by the results of the proficiency tests. The Center regularly participates in the certification of foreign-produced CRMs, including the European Union (ECRM). The results show good consistency with the results obtained by European laboratories.

500 - 600 enterprises of Russia, neighboring countries (Kazakhstan, Ukraine, and Belarus) and non-CIS countries (China, Germany, Japan, Georgia) buy our CRMs annually. The volume of export of CRMs increased in recent years; however, it is no more than 5% of the total revenues.

THE PRACTICAL USE OF REFERENCE MATERIALS FOR VERIFYING MEASURING INSTRUMENTS

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Keywords: CRM, reference material, thermophysical measurements, measuring instrument, metrology

The industrial production growth and the quality of the materials produced invariably leads to the need to create and improve existing instruments. As a result, quantity of the measuring instruments is expanding, which, according to an approximate assessment, 10% annually [1], verification of which is carried out with the help of certified reference material (CRM). These CRMs are used for verification and calibration of measuring instruments in various industries, from metallurgy to light and food industry.

A differential scanning calorimeter (DSC) is used to accurately measure and record the temperature of the structural transformations. More than 30 types of differential scanning calorimeters are entered in the state register. Basically, the model range is represented by the companies Netzsch-Geratebau GmbH (Germany), Mettler-Toledo GmbH (Switzerland), TA Instrument (USA), PerkinElmer LLC (USA).

In the course of preparation of these devices for research, sets of certified reference included in the device are used. Verification of the data of measuring instruments is usually carried out using a set of CRM of the melting point and the specific heat of fusion, consisting of pure metal reference materials (table 1). The unit of measurement is transferred from the standard to the working measurement tool using this set of CRM. The service life of this kit is not limited, but during operation the total stay at the phase transition temperature should not exceed 4 hours.

T a b l e 1. A set of CRM of the melting point and the specific heat of fusion

The name of the metal	The Number Of The State Register of Measuring	Melting point, K	The specific heat of fusion, kJ/kg
gallium	2312	303,04	-
indium	2313	429,85	28,58
tin	2314	505,20	59,92
zinc	2315	692,71	-
antimony	2316	903,76	-

Based on the analysis of the verification methods of measuring instruments, the main characteristics determined during the verification process are the temperature and specific heat of fuision given in table 1 .

The use of CRM for verification requires not only the skills of the verifier, but also the presence of the customer of additional funds for verification, not included in the standard set of most devices. Moreover, the lack of these funds often makes the verification process impossible.

Verification is preceded by the procedure of setting up the measuring instrument, according to its operating manual. The owner of the equipment carries out this procedure with the use of available complete certified reference of CRM remaining from the previous verification procedure. Frequent calibration on the previously used material, due to the absence of the approved type of CRM user, leads to incorrect setup and, as a result, negative results in the verification of measuring instrument. In view of such problems, it seems rational to include reference materials that are

supplied with measuring instrument in the state register. This will significantly reduce the time of verification, as well as the cost of the owners of measuring instrument to buy reference materials and increase the accuracy of the settings.

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“REFERENCE MATERIALS”: A SCIENTIFIC JOURNAL IN THE FIELD OF DEVELOPMENT AND USE OF REFERENCE MATERIALS

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“Reference Materials” is a quarterly, reviewed scientific and technical journal that has a thematic focus. The journal publishes results of basic and applied research of specialists working in the sphere of metrology and analytical chemistry, related to the issues of reference materials for composition and properties of substances and materials.

The main purpose of the journal is to provide an open platform for the exchange of scientific and practical information related to:

- development, production, use and comparison of reference materials;
- modern methods for analysis of substances and materials (chemical and physico-chemical methods, atomic and molecular spectroscopy, chromatography, X-ray spectroscopy, mass spectrometry, nuclear-physical methods of analysis, etc.);
- measurement capabilities in the field of analytical chemistry;
- metrological assurance of chemical analysis.

The journal accepts for publication: editorials and original articles; analytical, scientific and research, scientific and methodological materials, as well as materials intended for consultation and information; translations of published articles from foreign journals (with the consent of the right holder for the translation and publication); reviews; commentaries and event reports.

The average time from a paper submission to the first journal decision is 3 days.

The target audience of the journal is researchers and practitioners, university lecturers, postgraduates, quality control laboratories, measurement laboratories, business representatives and all interested in the field of reference materials.

The journal provides free access to its content, following the principle that: free access to research results contributes to increased information exchange. Publication, content archiving and receipt of full-text access in electronic form is free for authors (except for advertising articles) and readers (platinum open access model). Printed version of the journal is available via subscription.

We invite you to familiarize yourself with the materials of the journal on the website www.rmjournal.ru and consider the possibility of publishing your materials in the journal “Reference Materials”.

BAYESIAN METHODS IN THE CERTIFICATION OF REFERENCE MATERIALS

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The evaluation of measurement data in the production and certification of reference materials is often complicated by several factors. In homogeneity and stability studies, the effect of measurement precision can lead to problems in quantifying effects arising from (batch) inhomogeneity or instability. Bayesian methods can often be employed to overcome these problems in the data evaluation. Compared to their frequentist counterparts, they characterise in a more comprehensive manner these effects. Models are presented for the evaluation of batch homogeneity and long-term stability, taking into account the precision information of the methods used. The outcome of these models is compared with models known from meta analysis and traditional analysis of variance.

Bayesian models combine prior knowledge with data to provide a posterior probability distribution, from which an estimate, standard uncertainty, coverage interval, among others, can be computed. Special attention is paid to how prior information in reference material production can be elicited and included in the evaluation of homogeneity and stability study data.

In reference material characterisation, often additional dispersion, that cannot be explained from the uncertainty calculation of the results, needs to be taken into account. It is shown how this extra dispersion can be evaluated using traditional meta-analysis and Bayesian methods.

It is concluded that in some instances Bayesian methods clearly outperform over traditional statistical methods. In most cases however, when the prior information is not too strong and therefore modelled by weakly informative probability density functions, frequentist and Bayesian methods provide broadly the same estimates and similar standard uncertainties when based on the same assumptions.

COMBINED MEASUREMENT UNCERTAINTY FOR *pH*-VALUES USING CERTIFIED REFERENCE MATERIALS IN POTENTIOMETRIC MEASUREMENTS WITH GLASS ELECTRODES

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Keywords: pH-measurement, hydrogen electrode, pH-glass electrode, Harned-cell, certified pH-reference materials, CRM, uncertainty, calibration, ISO-GUM

The practical realisation of pH-measurements with Harned-cell type equipment used for the measurement of primary standards as recommended by IUPAC is shortly outlined.

In contrast to the Harned-cell without transference, the glass electrode with a junction is preferred and more practical for field laboratories. The combined measurement uncertainty is evaluated step by step in a systematic way according to ISO-GUM for a sample pH-value measured using a glass type electrode system, that was calibrated with two certified pH-reference material solutions.

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THE ACTIVITY OF A SPECIALIZED ORGANIZATION OF THE STATE SERVICE FOR REFERENCE MATERIALS OF VNIITSVETMET INSTITUTE

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Keywords: specialized organization, reference material of the composition, reference material category, reference material register, solid and dispersed material, control of the accuracy of measurements result, ensuring the uniformity of measurements

For implementation of the Order No.2 dd. January 8th, 2002 "To create the service of reference materials of the composition and properties of substances and materials" to perform the work, connected with the development and implementation of reference materials in the Republic of Kazakhstan, the chapter "the Specialized organizations of the State service for reference materials of the composition and properties of substances and materials of the Republic of Kazakhstan" was created in the register of the State system for ensuring the uniformity of measurements, where VNIItsvetmet Institute is registered as the specialize organization of the State service for reference materials (the SO SSRM).

The presence of human resources, industrial facilities, technological equipment, regulatory documents and also many years', since the 1970s, experience in development and production of reference materials of the composition, contributed the creation of the SO SSRM on the basis of VNIItsvetmet Institute.

The structure of the SO SSRM of VNIItsvetmet Institute includes the following divisions:

– The laboratory of standardization and metrology;

– Chemical and analytical laboratory;

– The laboratory of spectral assay.

The SO SSRM of VNIItsvetmet Institute in its activity is guided by [1], regulatory and legal documents, adopted by the Interstate Committee for Standardization, Metrology and Certification, and regulatory documents in the field of ensuring the uniformity of measurements [2, 3], and also the Regulations on the SO SSRM of VNIItsvetmet Institute.

Scientific and methodological guidance and coordination of activities of the SO SSRM in terms of development, producing and application of reference materials is performed by the Main Center of reference materials in accordance with the requirements [4].

Main objectives, functions, rights and obligations of the SO SSRM of VNIItsvetmet Institute meet the requirements [5].

One of the main objectives of VNIItsvetmet Institute, as the specialized organization of the SSRS, is development of reference materials of the composition of substances and materials and providing them to the enterprises of mining and smelting complex and scientific-research organizations of the countries from the Near and Far Abroad, and also to the Test Center of the Institute.

Reference materials are prepared by the level of recognition and assignment of the corresponding category:

– interstate (IRM);

– state (SRM);

– enterprise (ERM).

Since 2002, the year of creation of the SO SSRM of VNIItsvetmet Institute, 11 types of reference materials with the category of SRM were produced, 5 types of which were recognized in the category of IRM and 3 types were entered in the register of reference materials of the COOMET CRM. Besides, 83 types of reference materials were entered in the register of reference materials.

At the present time, the list with valid reference materials of the institute includes in total 24 SRM types and 52 ERM types.

For reference, there is given the list of reference materials under development:

– complex ores;

– products of complex ores beneficiation (concentrates, flotation tailings and middlings);

– metallic lead;

– metallic zinc;

– metallic cadmium;

– lead-antimonous alloys;

– zinc alloys;

– middlings of metallurgical production (fumes, cakes, dusts, etc.).

For reference, there are given several photographs of reference materials of the composition of solid and dispersed materials.

Fig.1. State reference materials for the composition of lead mark C0-C3 (set No. 1)
KZ.03.01.00057-2007

Reference materials are produced as solid materials in form of bars with the diameter of 10 mm and height of 100 mm.

Fig. 2. State reference materials for the composition of metallic cadmium mark Кд0А-Кд1 (set)
KZ.03.01.00001-2003 (IRS 0633:2004)

Reference materials are produced as solid materials in form of cylinders with the diameter of 40 mm and height of 25-30 mm.

Fig. 3. State reference material for the composition of gas duct dust during lead and zinc production
KZ.03.01.00076-2008
(the COOMET CRM 0062-2008-KZ)

Reference materials is produced in form of powdered material.

Reference materials of the composition are necessary to ensure the uniformity of measurements and quality control of the products, raw materials and materials in the production process. Enterprises-clients, who are interested in compliance of reference materials’ matrix with the matrix of the controlled materials, supply the initial raw materials to the Institute. From 2002 to 2018 the initial raw materials were received from the enterprises of the Republic of Kazakhstan, the Russian Federation and Kyrgyzstan.

Main consumers of the products are “Kazzinc” LLP (the Republic of Kazakhstan), “Kazakhmys Corporation” LLP (the Republic of Kazakhstan), “Electrozinc” OJSC (the Russian Federation), “The Tula Cartridge Works” JSC (the Russian Federation), “Kamskiy kabel” LLC (the Russian Federation), “Kharkov accumulator factory Vladar” LLC (Ukraine), etc., and also enterprises processing reference materials with help of companies of intermediary services.

So, reference materials play a key role in increasing competitive ability of the products in the world market by ensuring the uniformity of measurements and, as a consequence, improving the quality of products.

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EVALUATING THE EFFECTIVENESS OF CORRECTIVE ACTIONS AT THE LABORATORY OF NON-DESTRUCTIVE CONTROL

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Keywords: corrective actions, quality control material, efficiency, non-destructive testing, measures, certified characteristics, quality control

According to the requirements [1], the laboratory shall have quality control procedures for monitoring of tests undertaken. Quality control data should be analyzed, where they are found to be outside pre-defined criteria, planned corrective actions should be taken, that is, a corrective action procedure should be developed in the laboratory. The procedure for corrective actions should include: cause analysis, selection and implementation of corrective actions, monitoring of the effectiveness of corrective actions.

A documented procedure for assessing the effectiveness of corrective actions using a quality control material (hereinafter QCM) in the laboratory of non-destructive testing was developed for laboratories participating in the interlaboratory comparison of the laboratory 265 of “UNIIM”.

QCM is a pipe butt welded joint made of carbon steel by the method of manual arc welding, with a diameter of 159 mm, a wall thickness of 8 mm and a length of 200 mm, the metrological characteristics of QCM are given in Table 1. The method for establishing a certified value is interlaboratory certification by [3]

T a b l e 1. Metrological characteristics QCM

Certified characteristics	Certified value, mm	Limits of the absolute error of the certified value for P = 0,95, ± Δ, mm
Distance from the control point to the defect with the maximum echo from the defect 1.	115,63	4,27
Depth of defect 1	6,63	1,05
The conditional length of the defect 1	16,64	4,6
Distance from the control point to the defect with the maximum echo from the defect 2.	333,38	6,84
Depth of defect 2	6,60	0,75
The conditional length of the defect 2	12,32	0,89

The scheme of the process of assessing the effectiveness of corrective actions is shown in Fig. 1.

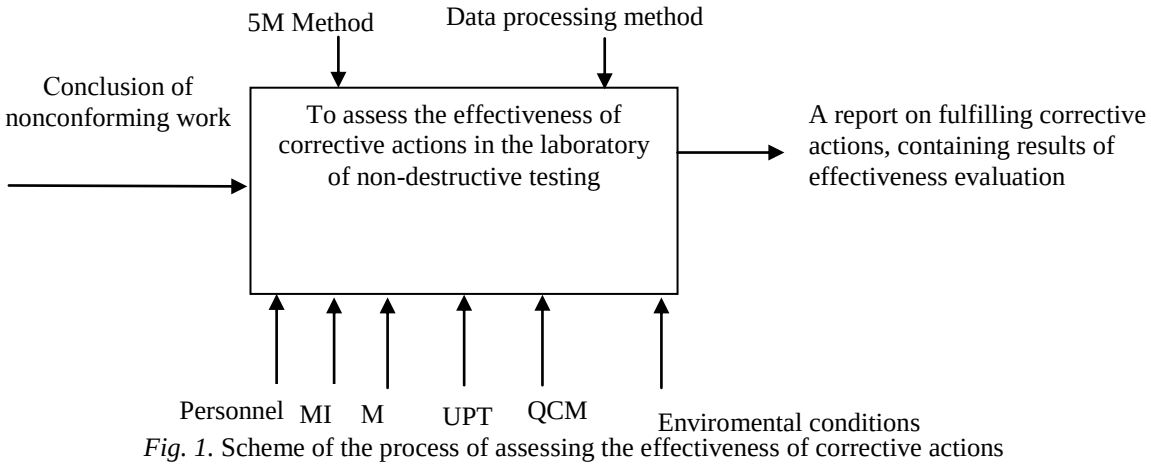

Fig. 1. Scheme of the process of assessing the effectiveness of corrective actions in the laboratory of nondestructive testing

A list of the causes of the inadequate measurement result was generated:

-Causes associated with the operator;

- the reasons connected with the measuring instrument (hereinafter referred to as MI);

- causes associated with ultrasonic piezoelectric transducer (hereinafter referred to as “UPT”);

-causes related to the method (hereinafter referred to as the M);

- the reasons connected with QCM;

- Reasons associated with measurement conditions.

The analysis of the reasons from the list is excluded:

- The reasons associated with the M, since the M is unified for use in the laboratory.

- Reasons associated with the QCM, because the QCM exists in a single copy.

- the reasons related to the enviromental conditions, since the measurement conditions are prescribed in the M and the control over the observance of the conditions is an integral part of the M.

A three-factor experiment has been developed that allows one to assess the effect of each of the causes of the inadequate measurement result. The essence of the experiment is that each of the three operators conducts the measurement of three MIs, sequentially connecting to each of the MI three UPTs. An algorithm for processing results by the variance method is given, according to [2]. The most influential is the reason, with the greatest value of the variance estimate, S.

Typical measures are established for each of the reasons for the occurrence of an inadequate measurement result.

A methodology for assessing the effectiveness of corrective actions is proposed. The measures taken to eliminate inconsistencies are considered effective if after an additional measurement the inequality is fulfilled, $|X - C| \leq \Delta_л$ where X is the result of the measurement, C is the assigned value of the QCM, $\Delta_л$ is the value of the interval estimation of the accuracy index of the measurement results, established when the technique is implemented in the laboratory and fixed by the laboratory protocol.

A form of a plan-report on the implementation of corrective actions was developed, including an indication of the reasons for the occurrence of an inappropriate measurement result with the degree of their influence, typical measures for each of the reasons, and the results of evaluating the effectiveness of corrective actions.

The developed documented procedure is an annex to the Instruction for the Application of the QCM.

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DEVELOPMENT OF A CERTIFIED REFERENCE MATERIAL OF HYDROGEN MASS FRACTION IN TITANIUM HYDRIDE

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Keywords: reference material, titanium hydride, mass fraction, hydrogen, inert gas fusion method, scientific research, metallurgy, nuclear power plant

Titanium hydride (II) has a wide industrial application: it can be used like a pore former for metal foam material production, a source of pure hydrogen, a catalyst in organic synthesis; it is useful for white sparks forming in pyrotechnics and like a component of a flux for soldering of metal with ceramics [1-3]. One of important use of titanium hydride (II) in industry is composite materials construction for biological protection of new type nuclear power plants against neutron radiation and also for radiological cabinets [4].

It is important to note that stoichiometric composition of titanium hydride (II) is stable only at 1 atm. pressure of hydrogen and 400 °C. At normal conditions this substance has variation in gross formula in range $TiH_{1,8}$ – $TiH_{1,99}$ and this leads to variation in properties of manufactured product.

All mentioned above and the absence of reference material of titanium hydride (II) composition in State register of approved types CRMs are show the necessity of metrological support for hydrogen mass fraction measurement in titanium hydride. This work is devoted to development of reference material of hydrogen mass fraction in titanium hydride.

The reference material may be used for validations of measurement procedure and checking an accuracy measurement results of hydrogen mass fraction in metal hydrides obtained by inert gas fusion method; calibration of hydrogen analyzers which use the inert gas fusion method; special procedure of including of measuring devices into the State register of approved types of measuring devices.

Fields of application of the reference material are scientific research, metallurgy, nuclear power industry, quality control of manufactured products.

For production of the reference material the fraction from 50 um to 2 mm of titanium hydride (manufactured by PO “Mayak”, Ozersk, Russia) have been used. Original material has been thoroughly cleaned and packaged into plastic vials with cap, mass of reference material 10 g.

Research of homogeneity and stability of the reference material has been made with taking into account the statements of GOST ISO Guide 35–2015 [5] and RMG 93-2015 [6]. All measurements in this work have been made according to measurement procedure M 251.1-2017 “Measurement procedure of hydrogen mass fraction in titanium hydride by inert gas fusion method” (certificate of attestation № 251.0310/RA.RU.311866/2017 from 04.09.2017, UNIIM).

Characterization and value assignment of properties of the reference material, evaluation of uncertainty and also error tolerance for certified value have been made with taking into account the statements of GOST ISO Guide 35–2015 and RMG 93-2015 and listed in Table 1.

T a b l e 1 Metrological characteristics of the reference material

Certified characteristic	Certified value, %	Relative error range of the certified value of the reference material (P=0,95), %	Relative expanded uncertainty of the certified value of the reference material at k=2 and P=0,95, %
Mass fraction	3,6	± 2,2	2,2

Developed reference material has been included into the State register of approved types CRM number of GSO 11021–2018.

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EXPERIENCE OF AN ACCREDITED LABORATORY IN INTERLABORATORY COMPARISONS

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Keywords: interlaboratory comparative tests, provider, participation evaluation, accreditation, accredited party, accreditation scope, minerals, gold-bearing ore, polymetallic ore, weight percentage, analyzed element

According to the section 5.9 of the GOST ISO/IEC 17025-20092009 [1] and the sections 23.11-23.11.1 of the Accreditation Criteria, testing laboratory shall participate in interlaboratory comparative tests (ICT) for independent evaluation of test validity. The Testing Analytical Center of Irgiredmet (TAC) have an accreditation as a testing laboratory since 1994 and wide experience in ICT programs of Russian and foreign providers, and if previously the range of programs and providers that complied with the TAC specialization was extremely limited, the situation is quite different now.

Since 2012, the number of ICT programs in which the TAC participated for embracing the entire accreditation scope has reached 21. In 2016, the “Rosacreditation Policy for Qualification Testing by Interlaboratory Comparative Tests” was approved that regulates participation in ICT programs for each test method in the field of accreditation of an accredited party at least once every five years. Thus, the TAC has reduced the number of ICT programs, in which it participates annually. In 2017, the TAC took part in seven programs; six programs have been planned for 2018.

The TAC regularly participates in ICT programs of foreign (ROCKLABS Ltd, New Zealand; Geostats Pty Ltd, Australia) and Russian providers (FSBI VIMS, the Minstandart research and development center, FSUE UNIIM, FSBI VNIIM, EZOCM etc.).

From 2013 to 2018, the TAC has participated in a range of testing projects for analysis of rocks; various ores and ore processing products; gold-containing activated carbon; gold alloys. These projects focused on measurements of weight percentage of SiO_2, Na_2O, MgO, Al_2O_3, P_2O_5, K_2O, CaO, TiO_2, MnO, Au, Ag, Pt, Pd, S_{tot}, As, Cu, Pb, Zn, Ni, Co, Fe, Cd, C_{tot}, V, Cr, Rb, Sr, Y, Zr, Mo, Sn, Sb, Ba, Bi, Ce, La, Ga, Cs, Th, U using the following methods: assay tests (gravimetric analysis, atomic absorption analysis, atomic emission analysis with inductively coupled plasma); X-ray fluorescence analysis, atomic absorption analysis, atomic emission analysis with inductively coupled plasma, mass spectral analysis with inductively coupled plasma; IR absorption analysis, gravimetric analysis, titrometric analysis. Measurements were carried out according to methods introduced in the TAC accreditation area (developed by Irgiredmet, FSBI VIMS, standard methods), developed by the TAC (for example, “Method of measuring total sulfur in samples of ores and products of ore processing by atomic emission spectroscopy with inductively coupled plasma” developed by the TAC in 2012) or introduced into the TAC analytical practice (for example, “Rocks, ores, products of processing. Determination of carbon by IR absorption analysis after burning in oxygen flow”, introduced in 2017).

Over the past five years, more than 2,500 measurement results have been obtained as a result of the TAC participation in ICT programs. The generalized evaluation of the quality of TAC participation results from 2013 to 2018 is shown in Figure 1. It demonstrates that 98.0 % of measurement results of the TAC were evaluated by providers satisfactorily. The analysis of ambiguous and unsatisfactory evaluations of results showed the presence of technical errors or their

non-systematic character (such evaluations were obtained for different elements in non-uniform programs of ICT), which indicates the random nature of obtained deviations.

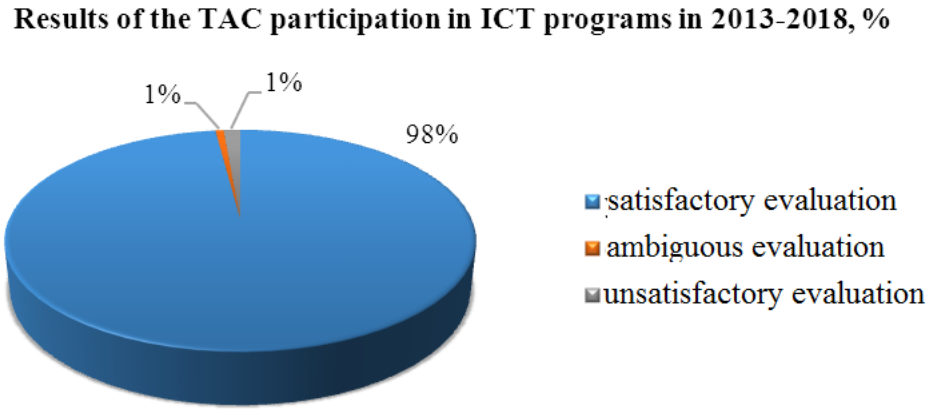

Fig. 1. General evaluation of the TAC participation in ICT programs in 2013-2018

Currently, the difficulties of participation of the TAC in ICT programs include:

- a limited number of ICT programs or their absence in relation to some measurement methods (for example, determination of carbon in organic compounds of rocks by IR absorption) and objects of measurement (for example, gold-bearing resins, platinum-containing ores, precious metals);
- a limited number of ICT providers accredited in the national system and consequently a lack of understanding with other providers regarding provision of information to the Rosaccreditation (RA) according to [3];
- different methods of participation evaluation in ICT programs from providers, which leads to difficulties in analyzing results;
- inevitable deviations from the Plan of Participation in ICT programs due to frequent changes in such plans by providers.
- lengthy delivery of samples from abroad, increasing the risk of disruption in delivery of results;
- as a consequence of all issues mentioned above, difficulties in planning TAC participation in ICT programs not only for five years (regulated by the RA), but even within one calendar year.

On the other hand, the wide experience of the TAC in participation in various ICT programs allows (in addition to obtaining an independent evaluation of measurement results reliability):

- to show relevance of applied measurement methods and level of competence of the TAC in comparison with equivalent laboratories in the Russian Federation and abroad;
- to assess correctness of application of new measurement methods at the TAC at the stages of their implementation and beginning of full use;
- to modernize measurement methods developed by the TAC, based on positive results of participation in ICT programs (expansion of measurement limits, changes in decomposition of samples);
- to confirm competence level of individual employees of the TAC, for example, trainees;
- to increase competitiveness of the TAC from the perspective of a customer by confirming reliability of results by an independent party;
- to draw the conclusion that there is a positive trend in terms of increasing objects and measurement methods in programs of ICT providers over the past five years.

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ON IMPROVING THE ACCURACY OF PRODUCING CERTIFIED REFERENCE MATERIALS OF IRON (III) AND COPPER (II) ION SOLUTIONS

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Keywords: certified reference material, calibration solution, traceability, direct primary method, controlled-potential coulometry, pure substances, copper (II), iron (III).

Certified reference materials (CRMs) of ion solutions are widely used in the sphere of state regulation of ensuring the uniformity of measurements. The first application is graduation and/or calibration of measuring instruments (MI), including specialized ones, intended for determining the ion content in aqueous media by different methods such as atomic absorption, spectrophotometric emission spectrometric, spectrometric, voltammetric, x-ray fluorescent and others. The other applications are monitoring MI metrological characteristics during their tests, including type approval, checking the accuracy of measurements and certification of the ion content measurement techniques in aqueous media.

National CRM producers are usually limited to concentration values of 10 g/dm^3 and 1 g/dm^3, whereas for a number of high-precision mass spectrometric and voltammetric methods, CRMs with concentrations less than 0.1 g/dm^3 are desirable (only two CRM producers manufacture CRMs with concentrations of 0.1 g/dm^3 and below). More over, the relative error of the certified value of 1 %, which 90 % of the producers declare, often does not allow using the CRMs for graduation and calibration of high-precision MI, especially when analyzing multicomponent solutions.

In the CRM Register there are not enough CRMs with metrological traceability to the State primary measurement standards of the units characterizing component content in substances. As a rule, certified measuring procedures or calculation-experimental method are used for establishing the certified value.

In 2016 UNIIM developed two CRMs which are reference measurement standards, being a part of the State primary measurement standard GET 176. These CRMs were certified by the primary method of controlled-potential coulometry. Their metrological characteristics are given in the table 1.

T a b l e 1. Metrological characteristics of CRMs for composition of high purity copper and high purity iron certified by the primary method of controlled-potential coulometry using GET 176

CRM number	CRM certified characteristic	CRM certified value, %	Expanded uncertainty of the certified value, $U_{(k=2)}$, %	The range of the absolute error of the certified value ±Δ, % (at P=0,95)
10800-2016 (Cu UNIIM GSO)	Copper mass fraction	99.994	0.012	0.012
10816-2016 (Fe UNIIM GSO)	Iron mass fraction	99.987	0.013	0.013

In 2017 UNIIM participated in the key comparison CCQM-K 143 "Comparison of copper calibration solutions prepared by National Metrology Institutes" conducted by the National Institute of Standards and Technology (NIST, USA) using CRM of high purity copper (Cu UNIIM GSO).

Copper calibration solution with a mass fraction of 9.9910 g/kg was prepared from GSO 10800-2016 with a relative expanded uncertainty of 0.17 % (including uncertainty due to stability for a 1 year).

This calibration solution was used to prepare standard solutions of copper (II) with concentrations of 1 g/dm^3 and 0.1 g/dm^3.

The solution of iron (III) with a concentration of 1 g/dm^3 was prepared by a gravimetric method, by dissolving a high-purity iron sample in special purity nitric acid according to the GOST 11125-84 "Nitric acid of special purity. Technical conditions", which was additionally purified by distillation using a vacuum unit for low-boiling distillation of acids.

The content of impurity elements in nitric acid was monitored by inductively coupled plasma mass spectrometry (ICP-MS) using a mass spectrometer NexIon-300D.

Solutions with concentrations of 0.1 g/dm^3 were prepared by a multiple dilution. Weighing of iron sample for dissolution, as well as aliquots of the prepared solutions, were carried out taking into account the corrections for the buoyancy of air using mass comparator CCE-66 ("Sartorius", Germany), accuracy class I (special), sampling resolution 0.000001 g. The density of obtained copper and iron solutions was measured using a liquid density analyzer DMA 4500M.

The prepared solutions were packaged in polyethylene cans (HDPE) with a capacity of 60 cm^3 with polypropylene lids from NALGENE. Uncertainty due to long-term instability during the storage of solutions for one year was investigated earlier and amounted to 0.064%.

Mass concentrations of the resulting solutions were calculated by the preparation procedure ($C_{cal.}$), and then measured using the State primary measurement standard GET 176-2017. Measurements of the mass concentration of copper in solutions of copper (II) ions and mass concentration of iron in solutions of iron (III) ions were performed using the reference installation implementing a controlled-potential coulometry (CCP) which is a part of the State primary measurement standard GET 176.

The copper measurement method is based on the reactions of electrochemical reduction of Cu^{2+} ions to Cu^{+} on a platinum grid at a potential of 0 mV and electrochemical oxidation of Cu^{+} ions to Cu^{2+} at a potential of + 480 mV in a 1 m hydrochloric acid medium.

The method of measuring iron is based on the reactions of electrochemical reduction of Fe^{3+} ions to Fe^{2+} on a platinum grid at a potential of +250 mV and electrochemical oxidation of Fe^{2+} ions to Fe^{3+} at a potential of +750 mV in a 1 m nitric acid medium.

The measurement results of the concentrations of the prepared solutions are given in the table 2.

The type A relative standard uncertainty of measuring the mass concentration units of the component was estimated as the relative standard deviation of the measurement results of 7 independent measurements. The type B relative standard uncertainty was estimated as a composition of the uncertainty components due to sample weighing (m), measuring the amount of electricity consumed in the electrolysis process (Q_α), determining the completion rate of the electrochemical reaction (K_c), molecular weight (m), the Faraday constant (F) [1]. Also, the uncertainty components associated with the electrolytic cell were refined: the effect of oxygen, impurities of the electrolyte, diffusion of the electrolyte into electrolytic keys (chambers). Uncertainties of the measurement results for solutions with mass concentrations of 10 g / dm^3 were investigated earlier [2].

T a b l e 2. Measurement results of mass concentration of copper in solutions of copper (II) ions and mass concentration of iron in solutions of iron (III) ions with a nominal concentration of 1 g/dm^3 and 0.1 g/dm^3 determined using the State primary measurement standard GET 176-2017

Sample number	Solution of copper (II) ions, $C_{cal.}$= 1,0375 g/dm^3	Solution of copper (II) ions $C_{cal.}$= 0, 1092 g/dm^3	Solution of iron (III) ions, $C_{cal.}$= 1,0001 g/dm^3	Solution of iron (III) ions, $C_{cal.}$= 0,1041 g/dm^3
	The mass concentration of copper, g/dm^3		The mass concentration of iron, g/dm^3	
1	1,03756	0,10927	0,99967	0,10382
2	1,03734	0,10925	0,99898	0,10390
3	1,03811	0,10934	0,99937	0,10385
4	1,03791	0,10935	1,00015	0,10404
5	1,03845	0,10927	0,99972	0,10393
6	1,03900	0,10929	0,99873	0,10381
7	1,03810	0,10934	0,99953	0,10396
The mean value, $\overline{C}$, g/dm^3	**1,0381**	**0,1093**	**0,9995**	**0,1039**
Type A relative standard uncertainty, u_A, %	0,020	0,014	0,018	0,030
Type B relative standard uncertainty, u_B, %	0,009	0,043	0,008	0,043
The combined relative standard uncertainty, u_c, %	0,022	0,045	0,020	0,053
The extended relative uncertainty (k = 2), U_0, %	0,044	0,091	0,040	0,105

The conducted studies showed that the use of a reference controlled potential coulometric installation as a part of the GET 176-2017 allows to establish the direct traceability of CRM certified values of the iron (III) and copper ion solutions to the primary measurement standard and to SI units, and to release the CRMs of the iron (III) and copper ion solution in the concentration interval from 0.1000 to 10.00 g/dm^3 with a shelf life of 1 year and the expanded uncertainty not exceeding 0.2 %.

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Alphabetical Index

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182