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ИЗМЕРЕНИЕ ПЛОТНОСТИ ЖИДКОСТИ В СИСТЕМЕ ОБЕСПЕЧЕНИЯ ЕДИНСТВА ИЗМЕРЕНИЙ

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Приведены результаты исследования, направленного на создание национального эталона плотности жидкости. Эталон обеспечивает воспроизведение, хранение и передачу единицы плотности жидкости в диапазоне от 650 до 2000 кг/м^3. На основе метода гидростатического взвешивания реализовано измерение плотности жидкости в соответствии с ГОСТ OIML R 111-1-2009 «Государственная система обеспечения единства измерений. Гири классов E_1, E_2, F_1, F_2, M_1, M_{1-2}, M_2, M_{2-3} и M_3. Часть 1. Метрологические и технические требования». Показано, что применение масс-компаратора высокой точности позволяет значительно снизить систематическую погрешность измерений и среднеквадратичное отклонение при воспроизведении единицы плотности жидкости и ее передаче эталонным средствам измерений 1-го и 2-го разрядов и рабочим средствам измерений. Реализован метод передачи единицы плотности жидкости посредством эталонной меры плотности – кремниевой сферы и жидкости-компаратора, что позволило исключить передаточное звено в виде эталонного раствора плотности жидкости. В диапазоне воспроизведения, хранения и передачи единицы плотности жидкости получена систематическая погрешность $2{,}1 \cdot 10^{-3}$ кг/м^3, среднеквадратичное отклонение при воспроизведении единицы плотности жидкости составило $4{,}0 \cdot 10^{-4}$ кг/м^3, среднеквадратичное отклонение суммарной погрешности при передаче единицы плотности жидкости равнялось $3{,}14 \cdot 10^{-3}$ кг/м^3.

Ключевые слова: эталон единицы плотности жидкости; метод гидростатического взвешивания; эталонная мера плотности; воспроизведение; хранение; передача единицы плотности жидкости.

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MEASURING LIQUID DENSITY IN A SYSTEM FOR ENSURING UNIFORMITY OF MEASUREMENTS

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The article presents the results of a study aimed at creating the national standard for liquid density. The standard provides reproduction, storage and transmission of the liquid density unit in the range from 650 to 2000 kg/m^3. Based on the method of hydrostatic weighing, the measurement of liquid density was implemented in accordance with the GOST OIML R 111-1-2009 «State system for ensuring the uniformity of measurements. Weights of classes E_1, E_2, F_1, F_2, M_1, $M_{1–2}$, M_2, $M_{2–3}$ and M_3. Part 1. Metrological and technical requirements». It is shown that the use of a high-precision mass comparator can significantly reduce the systematic measurement error and the standard deviation when reproducing and transferring the unit of liquid density to reference measuring instruments of the 1st and 2nd category and working measuring instruments. A method for transferring a unit of liquid density by means of a standard density measure – a silicon sphere and a comparator liquid – has been implemented, which made it possible to exclude the transfer link in the form of a standard liquid density solution. In the range of reproduction, storage and transmission of the liquid density unit, a systematic error of $2.1 \cdot 10^{-3}$ kg/m^3 was obtained, the standard deviation in the reproduction of the liquid density unit was $4.0 \cdot 10^{-4}$ kg/m^3, the standard deviation of the total error in the transmission of the liquid density unit $3.14 \cdot 10^{-3}$ kg/m^3.

Keywords: liquid density unit standard; hydrostatic weighing method; density standard measure; reproduction; storage; transfer of liquid density unit.

Introduction

Since 13 January 2020, Belarus is a full-fledged member of the Metre Convention – an agreement to ensure uniformity of metrological standards, the signatories to which are currently 62 states all around the world.

Signing the Metre Convention imposes certain requirements on signatory states. One of the requirements is to establish and develop a country-wide system for ensuring uniformity of measurements. The origins of the national system for ensuring uniformity of measurements in the Republic of Belarus date back to the 1990s, the time of the early creation of the national system of measurement standards for physical quantities. The crucial role in these activities has been played by the Belarusian State Institute of Metrology, which, in accordance with the Law of the Republic of Belarus «On ensuring uniformity of measurements», has the mandate by the State Committee for Standardisation of the Republic of Belarus to act as the country's National Metrological Institute. When working on establishing measurement standards, BelGIM cooperates closely with the National Academy of Sciences of Belarus and leading domestic universities. Now, there are a total of 65 national measurement standards representing units of physical quantities.

Development of new cutting-edge technologies drives a need for using measuring instruments that have a substantially better resolution, for reducing measurement errors of methods and instruments, as well as for stronger automation and higher operation rates of the latter. The metrological characteristics of measuring instruments improve continuously, so the accuracy of measurements. This, however, poses a general question regarding highest available accuracy of determination of values of various physical quantities when using high-precision instruments and urges for verification and demonstration of their proper metrological characteristics.

Liquid density measurements are widely applied across industries, since density represents not only a quantitative, but also a qualitative characteristic of a raw material. Density data are fundamental for investigation of properties of liquids, their identification, and determination of their purity grade. These are also required for indirect evaluation, with a certain degree of accuracy, of some other liquid properties, like specific weight, thermal expansion or contraction, mass of a known volume of liquid, etc.

A unit of density is a physical indicator of a characteristic determined for substances of a homogeneous nature (liquid, solid, gaseous) using their mass per unit volume. According to the International System of Units, a unit expressed in kilogram per cubic meter is used to determine density indicators. Density values for various materials are in fairly wide measurement ranges. The ability to determine the density of substances in liquid and solid states is called densimetry.

The density characteristic of any substance depends on the mass of atoms that are part of this substance and on the density of the arrangement of compounds of atoms, as well as molecules in this substance.

For liquids, the determination of density is important for two reasons. The first is to assess the liquid from the qualitative side, when checking its density, they look at the compliance of the liquid with the standards of quality indicators. Such changes are made in the laboratory. The second reason for determining the density is to calculate the mass of the liquid. Since when the temperature changes, there is no change in the mass of the liquid, it is customary to take into account the amount of liquid not by volume, but by mass.

Various methods exist for characterising the densities of liquids. A large group consists of float-weight methods based on determining the buoyancy force acting on a body or an auxiliary element – a float and, according to the Archimedes' principle, having a directly proportional dependence on the density of the medium. This group includes measurements with a hydrometer, by means of hydrostatic weighing, float, flotation methods for determining density.

The next group includes hydrostatic methods for determining the density characteristic, which determines the dependence of the static pressure of a liquid or gas column of constant height on their density.

The following measurement methods are typical for determining the density of liquid substances:

• *buoyancy method (areometric)*[1]. To implement these methods, the body, which is pressed by a force equal to the weight of the fluid displaced by the body, is partially or completely immersed in the fluid. This method is implemented using float density meters (hydrometers):

– having a floating float and measuring the depth of its immersion;

– equipped with a submerged float and measuring the force acting on the float.

The basis of the hydrometer is Archimedes' principle.

There are hydrometers with constant volume and hydrometers with constant mass. Density is determined by the mass of the load (weights) and based on the volume of liquid displaced.

The above method is widely used in practice in order to determine the relative density of ethyl alcohol and acids (sulfuric, nitric and hydrochloric). Analyses using this method are performed quickly, which refers to its positive aspects. It can also be used to analyse liquids with a fairly high viscosity. However, the measurement accuracy of this method leaves much to be desired, which refers to its disadvantages, and a relatively large amount of liquid is also required for measurements;

• *hydrostatic weighing method*[2]. This method is used for mass determination of density in cases where simplicity of the process and speed of its implementation are preferred, or in the case when work is carried out at high pressures. Hydrostatic balances are widely used to determine the density of liquids. The advantage of these devices is the fact that a rather small amount of liquid or substance is required to determine the density characteristic with their help;

• *flotation method for determining the density*[3]. This method is characterised by the fact that a float immersed in a liquid is brought to a state of equilibrium, the so-called flotation equilibrium. He won't be able to float and he won't be able to sink. Flotation equilibrium is characterised by the equality of the densities of the float and liquid. When determining the density of the float and the corresponding temperature of flotation equilibrium, the density of the liquid at a given measurement temperature is also determined. The magnetic float flotation method is currently being developed and mastered as part of the use of electronic tracking systems that automatically maintain the float at the desired height. Keeping the float stationary relative to the cuvette prevents the viscosity of the liquid and the walls of the cuvette from being affected. A fairly small volume of liquid is needed for the density determination process;

• *pycnometric method*[4]. In laboratories of chemical industries and pharmaceutical plants, when conducting technical analyses, pycnometers (volume-weight density meters) are usually used along with hydrometers. The principle of operation of these meters is that the mass of a substance is directly proportional to the density at a constant volume of this substance. To determine the density, it will be sufficient to continuously weigh a certain volume of liquid flowing through the pipeline. The advantages of these devices are that they can determine the density of pulps, suspensions, liquids (high degree of contamination, viscous and volatile); readings do not depend on the flow time of the liquid and its properties; they can determine the density at high pressures (maximum 2.5 MPa); the measuring cavity of the device has a constant cross section, which

[1]GOST 3900-85. Petroleum and petroleum products. Methods for determination of density. Interstate standard. Introd. 01.01.1987. Mosc. : Stand. Publ. House, 2000. 140 p. ; GOST 8.428-81. State system for ensuring the uniformity of measurements. Areometers. The values of coefficients of surface tension of liquids (amendment 1). Introd. 01.07.1982. Mosc. : Stand. Publ. House, 1986. 10 p. ; GOST ISO 3675-2014. Crude petroleum and liquid petroleum products. Laboratory method for determination of density by hydrometer. Introd. 01.01.2017. Mosc. : Standartinform, 2019. 12 p.

[2]OIML G 14. Guide. Edition 2011 (E). Density measurement. Introd. 01.09.2011. Paris : OIML, 2011. 29 p.

[3]GOST 15139-69. Plastics. Methods for the determination of density (mass density). Introd. 01.07.1970. Mosc. : Stand. Publ. House, 1988. 17 p.

[4]ISO 2811-1:1997. Paints and varnishes. Determination of density. Part 1. Pyknometer method (MOD). Introd. 01.07.2014. Geneva : International Organization for Standardisation, 1997. 9 p.

prevents the deposition of solids from the flow, they have high sensitivity parameters and high measurement accuracy; the measurement range of these devices is adjustable over a wide range (100–2000 kg/m^3);

• *method based on the determination of pressure*[5]. The pressure difference between two liquid levels is determined. When maintaining a constant liquid level, the pressure below the surface of the liquid indicates its density. It is possible to measure the pressure difference between two different liquid levels. This difference is directly proportional to the density of the liquid. This method is called the «wet-pipe» method, which contains a separating fluid whose density is higher than that of the working fluid being measured. If it is not possible to use a separation fluid, a pressure repeater is used to reproduce the pressure in the upper level and allow the instrument to monitor the pressure difference between the liquid levels;

• *vibrating methods*[6]. A mechanical vibrator in the shape of a U-tube oscillates at its resonant frequency, which depends on its mass. When the device is introduced into the sample of the investigated liquid, the resonant frequency of oscillations changes. The instrument should be calibrated using two standard liquids of known density. Standard fluids are selected so that their densities cover the range within which the expected density of the test fluid falls;

• *ultrasonic methods*[7]. Ultrasound is used to determine the density of a substance. An ultrasonic vibration in a medium can be created by any oscillating body that is in contact with this medium. To determine the density index in this medium, it will be necessary to determine the speed of propagation of ultrasound in it. This is a highly sensitive method, almost completely inertialess and eliminates contact with the controlled environment, which means it can work in aggressive environments.

Newly mastered measurement methods are gaining great popularity, associated with the use of certain physical phenomena and the use of quantities that uniquely depend on density, for example, the attenuation of radioactive radiation, the speed of sound propagation in a substance, the frequency and amplitude of oscillations of a vibrating auxiliary body, parameters occurring in a fluid flow or vortex gas.

The accuracy of parameters in determining the density characteristic is of great importance in the development and production of measuring instruments in various industrial fields, such as instrumentation and metrology, which are closely related to the analysis of the properties of certain substances and materials.

A wide variety of methods for measuring the density of a liquid raises the question of creating a standard for the density of a liquid, which can reproduce, store and transmit a unit of liquid density to measuring instruments and standard samples, ensuring the uniformity of liquid density measurements with high accuracy.

Materials and methods

To ensure uniformity of measurements in the field of densitometry pursuant to task 2.14 «Establishing a new national measurement standard for liquid density» within the scope of the sub-programme «Measurement standards of Belarus» of the state scientific and technical programme «Development and manufacture of Belarusian measurement standards, proprietary instruments and facilities for scientific research (national measurement standards and scientific instrumentation)», BelGIM in the years from 2018 to 2020 established a new National measurement standard of liquid density (NE 61-21). The standard is designed for realisation and maintenance of the liquid density unit (kg/m^3), and its further dissemination to appropriate 1st grade working standards. There is a large variety of methods to determine liquid density nowadays. Basically, these can be divided into two main groups, i. e. indirect and direct ones. The most known indirect methods are the pycnometric and the hydrostatic weighing method. The difference is that when applying the pycnometric method the liquid density is being determined by using a container of a constant capacity, while for the hydrostatic weighing a constant mass reference measure shall be used.

We have chosen the hydrostatic weighing as the preferred method for liquid density determination. The essence of the method is that the density of a liquid is being measured based on the Archimedes' principle. When measuring the liquid density, a body of known mass and volume is being weighed while immersed in the liquid.

The measure we use to realise and maintain the liquid density unit by means of the hydrostatic weighing method is a Si-sphere (hereafter called the «sphere») (*Häfner*, Germany). The sphere is made of 1 kg of high-purity silicon.

[5]ISO 2811-4:2011. Paints and varnishes. Determination of density. Part 4. Pressure cup method. Introd. 01.03.2011. Geneva : International Organization for Standardisation, 2011. 16 p.

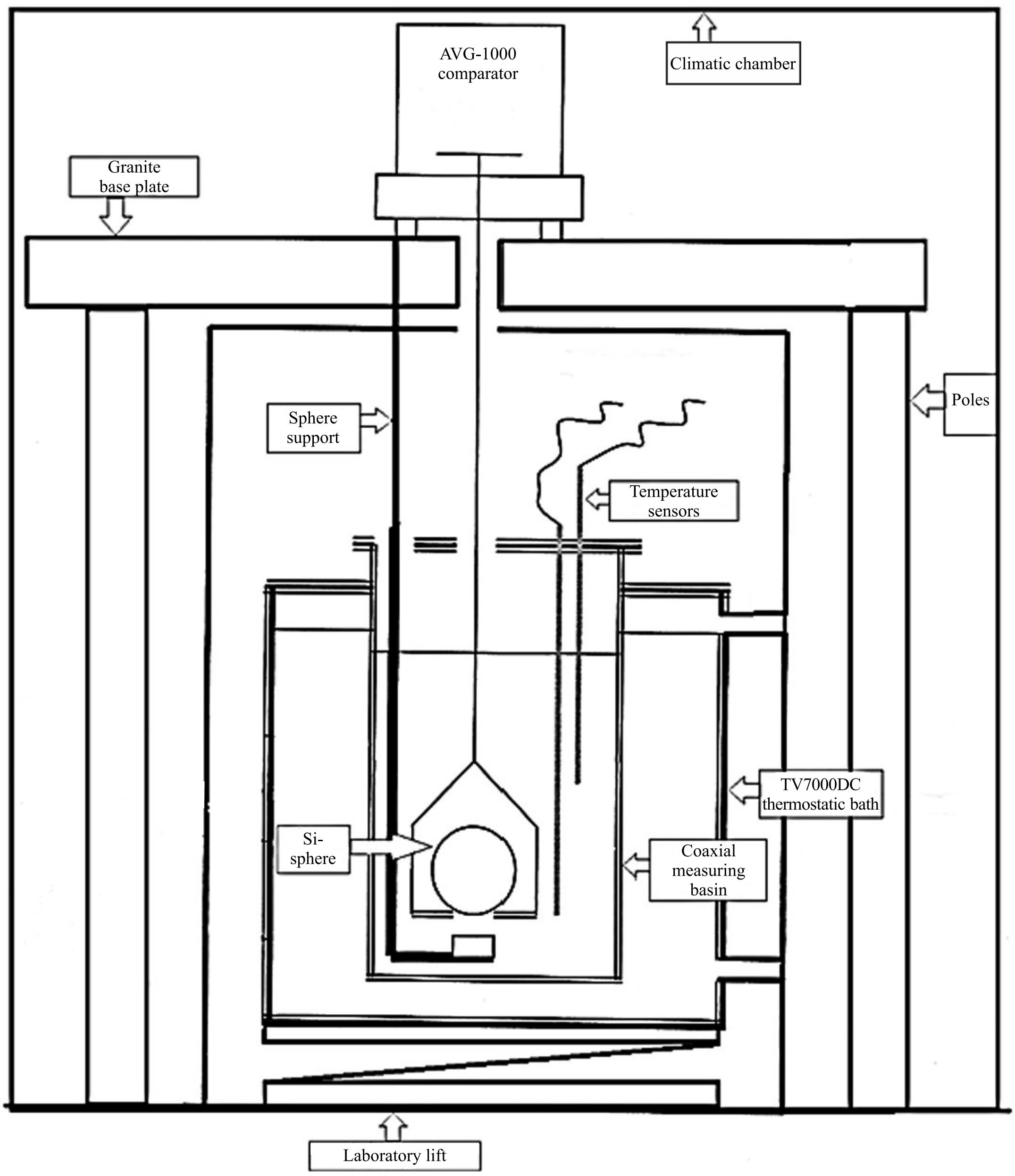
[6]GOST 33453-2015. Testing of chemicals of environmental hazard. Determination of the density of liquids and solids. Introd. 01.09.2016. Mosc. : Stand. Publ. House, 2016. 6 p.

[7]Shaverin N. V. Development of an ultrasonic method and means of automated control of the density of petroleum products : abstr. of a dissertation … candidate of technical sciences : 05.11.13. Tomsk : Natl. Res. Tomsk Polytech. Univ., 2003. 20 p.

The algorithm applied for the realisation of the liquid density unit is implemented in accordance with the conventional scheme by using an AVG-1000 high-precision hydrostatic weighing mass-comparator (hereafter called the «comparator») (*Radwag Wagi Elektroniczne*, Poland)[8]. The sphere is first weighed in the air on the comparator pan. For temperature conditioning, a CCK-0/7702m test chamber (*Dycometal Equipos de Control de Calidad*, Spain) is used, namely in conjunction with a THB-Box communicator with THB P sensors (*Radwag Wagi Elektroniczne*), which allows very accurate measurements of the environmental parameters.

After that, the sphere is placed on the lower weight holder of the comparator; then a TV7000DC thermostatic bath (hereafter called the «bath») (*Tamson Instruments B. V.*, Netherlands) is lifted up towards the comparator by means of a lifting gear. The coaxial measuring basin of the bath contains the liquid under investigation. Once temperature stabilised, the sphere is weighted in the liquid. The temperature of the liquid under investigation is monitored by E20 Thermometer temperature meters (*Radwag Wagi Elektroniczne*).

A diagram depicting the set-up for the realisation of the liquid density unit is shown in figure.



Implementation scheme of the standard

[8]GOST 8.428-81. State system for ensuring the uniformity of measurements. Areometers. The values of coefficients of surface tension of liquids (amendment 1). Introd. 01.07.1982. Mosc. : Stand. Publ. House, 1986. 10 p.

The density of the liquid under investigation is calculated by the formula

$$\rho_l = \frac{\left(C_a m_{ra} + \Delta m_{wa} - C_{al} m_{rl} - \Delta m_{wl}\right)\rho_t + \rho_a\left(C_a m_{rl} + \Delta m_{wl}\right)}{\left(C_a m_{ra} + \Delta m_{wa}\right)\left(1 + \beta_{sphere}\left(t_{vl} - t_{cl}\right)\right)}, \quad (1)$$

where C_a is the correction for the effect of buoyancy in air (air density) at the time of weighing the sphere in the air; m_{ra} is the mass of the sphere, kg; Δm_{wa} is the mass difference when weighing the sphere in the air, kg; C_{al} is the correction for the effect of buoyancy in air (air density) at the time of weighing the sphere in the liquid; m_{rl} is the mass of the technical weight, kg; Δm_{wl} is the mass difference when weighing the sphere in the liquid, kg; ρ_t is the density of the sphere, kg/m^3; ρ_a is the air density, kg/m^3; β_{sphere} is the volume expansion coefficient of the sphere, K^{-1}; t_{vl} is the actual temperature of the liquid the density of which is being determined, °C; t_{cl} is the certification temperature of the liquid the density of which is being determined, equal to 20 °C.

The liquid density value resulting from the measurements and calculations above is compared with a standard set of reference values to allow for identification of the liquid under investigation.

When disseminating the density unit to 1st grade working standards, a XA210/Y laboratory hydrostatic weighing balance with a lower weigh holder (hereafter called the «balance») (*Radwag Wagi Elektroniczne*) is used.

A 1st class working standard is secured at lower weigh holder of the balance and weighed in the air. Then, further weighing is carried out in the liquid, the density of which is given by formula (1). By means of a lift gear, the container is raised gradually until the liquid level is aligned with the lower mark of the hydrometer scale. When the set-up has been thermally stabilised, weighing in the liquid is conducted sequentially at all numbered scale points of the 1st grade working standard.

The actual density value ρ_{ACT} (in kg/m^3) at a given scale point is calculated by the following formula:

$$\rho_{ACT} = \frac{\left(M_{HA} + m'\right)\left(\rho_{vl} - e_l\right)}{\left(\left(M_{HA} - M_{HL}\right) + m\right)\left(1 + \beta_{he}\left(t_{cal} - t_{vl}\right)\right)} + e,$$

where M_{HA} is the mass of the hygrometer in the air, kg; m' is the mass of the meniscus around the hydrometer rod at the given scale point in the liquid for which the hygrometer is routinely used, kg; ρ_{vl} is the liquid density, kg/m^3; e_l is the air density when weighing the hygrometer in the liquid, kg/m^3; M_{HL} is the mass of the hygrometer in the liquid, kg; m is the mass of the meniscus around the hydrometer rod at the given scale point in the liquid, kg; β_{he} is the volume expansion coefficient of the hydrometer glass, K^{-1}; t_{cal} is the calibration temperature of the hydrometer, equal to 20 °C; t_{vl} is the actual temperature of the liquid, °C; e is the air density when weighing the hygrometer in the air, kg/m^3.

The mass of the meniscus around the hydrometer rod at the given scale point in the liquid m (in kg) is calculated by the formula

$$m = \frac{\pi d \sigma}{g},$$

where d is the diameter of the hydrometer rod at the given scale point, m; σ is the surface tension coefficient of the liquid, mN/m; g is the gravitational acceleration, m/s^2.

Also the mass of the meniscus around the hydrometer rod at the given scale point in the liquid for which the hydrometer is routinely used m' (in kg) is calculated by the formula

$$m' = \frac{\pi d \sigma'}{g},$$

where σ' is the surface tension coefficient of the liquid for which the hydrometer is routinely used, mN/m.

The appropriate surface tension coefficient values are thoroughly established and well known for various liquid types[9].

The liquid density standard is operated by custom software that has been developed as a part of the task activities.

When determining the residual systematic error of the measurement standard for liquid density, the following components are considered:

– expanded uncertainty of mass measurements of the sphere;
– expanded uncertainty of volume measurements of the sphere;
– expanded uncertainty of temperature measurements of the liquid.

[9]GOST 8.024-2002. State system for ensuring the uniformity of measurements. State verification schedule for means of measuring density. Introd. 01.03.2003. Mosc. : Stand. Publ. House, 2003. 9 p.

The residual systematic error Θ (in kg/m^3) of the liquid density standard is calculated by the formula

$$\Theta = \pm\sqrt{\sum_{i=1}^{m}\Theta_i^2},$$

where Θ_i is the limit of the i residual error component, 10^{-3} kg/m^3; m is the number of residual systematic errors added together.

The root-mean-square deviation of the measurement results is calculated by the formula

$$S = \sqrt{\frac{\sum_{i=1}^{n}\left(\rho_i - \overline{\rho_j}\right)^2}{n-1}},$$

where ρ_i is the i observation of the j input quantity, 10^{-3} kg/m^3; $\overline{\rho_j}$ is the result of the measurement of the j input quantity (arithmetic mean of corrected observations) determined by formula (in 10^{-3} kg/m^3)

$$\overline{\rho_j} = \frac{\sum_{i=1}^{n}\rho_i}{n},$$

where n is the number of observations of the j input quantity, $n = 10$.

Results and discussion

The outcomes of the investigation of the metrological characteristics of the liquid density standard are given in table.

Metrological characteristics of the standard

Characteristic	Value, kg/m^3
Liquid density measurement range	650 to 2000
Residual systematic error of the realisation of the liquid density unit	$2.1 \cdot 10^{-3}$
Root-mean-square deviation of the realisation of the liquid density unit	$4.0 \cdot 10^{-4}$
Root-mean-square deviation of the total error of the dissemination of the liquid density unit	$3.14 \cdot 10^{-3}$

The results obtained prove that the metrological characteristics of the recently developed liquid density standard fulfill the requirements prescribed in the design specification and are also in line with the similar metrological characteristics of the liquid density standards used in other countries.

Conclusion

The present extension of the measuring capabilities of the standard is due to ongoing investigation of its characteristics, enlargement of the list of liquids to be examined, participation in international comparisons, and improvement of the method of how the liquid density unit can be disseminated to a 1st grade working standard[10].

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[10]GOST OIML R 111-1:2009. State system for ensuring the uniformity of measurements. Weights of classes E_1, E_2, F_1, F_2, M_1, M_{1-2}, M_2, M_{2-3} and M_3. Part 1. Metrological and technical requirements. Introd. 01.07.2012. Mosc. : Standartinform, 2019. 97 p.