ERRATA

Erratum: “Standard Samples in the Quality System for Measurements in Analytical Chemistry” [*Inorganic Materials*, 2008, Vol. 44, No. 14, pp. 1595–1598]¹

I. E. Dobrovinskii, E. V. Osintseva, G. I. Terent'ev, and A. V. Skutina*

FGUP UNIIM, Yekaterinburg, Russia

*E-mail: avs@uniim.ru

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Abstract—Problems of providing measurement quality in analytical chemistry using reference materials certified by primary methods are considered in this paper. We describe a scheme of establishing the traceability of measurement results in a chemical composition of substances to SI units, exemplifying it by reference materials, certified in FGUP “UNIIM” by a primary method—coulometric titration technique.

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At present, under conditions of creating a universally acceptable measurement system, the greatest importance is given to the quality of measurements, obtaining reliable results, and presenting them in established units. In a multistage process of determining chemical composition of substances and materials, comprising the stages of sampling, sample preparation, selection of methods and means of measurement, conducting measurements in compliance with established procedures, and processing of the obtained results, the measurement quality, as a whole, is determined by establishing the traceability of measurement results to SI units.

Establishment of traceability of measurement results to the SI units, as a crucial condition for ensuring the uniformity of measurements, is one of the most important issues on the agenda of forums of international organizations, such as International Organization for Standardization (ISO), International Union of Pure (Theoretical) and Applied Chemistry (IUPAC), Cooperation for International Traceability of Measurements in Analytical Chemistry (CITAC), and International Laboratory Accreditation Cooperation (ILAC). In the absence of the mole measurement standard, the traceability of measurement results to the SI units in analytical chemistry is, as a rule, realized by means of reference materials (RMs) of the composition of high-purity substances which are certified against measurement standard or by other means. In general, for establishing the traceability of certified reference materials, the following ways of their certification may be used:

- using primary methods;
- using certified methods of comparison;

– by preparation procedure.

In accordance with the definition of the Consultative Committee for Amount of Substance (CCQM) of the International Committee for Weights and Measures, “a primary method is a method having the highest metrological qualities, whose operation can be completely described and understood and for which full uncertainty can be written in terms of SI units” [1]. Primary methods do not require any preliminary calibration with the use of certified reference materials.

ISO/REMCO Guide 35 [2] specifies as primary the following methods:

– Gravimetry (*measurement of mass*)—this method is suitable for assessing the degree of purity of a substance, as well as for determining the content of macrocomponents in a sample.

– Coulometry (*measurement of mass by means of measuring the quantity of electricity according to Faraday's law*)—this method is used for assessing the degree of purity of a substance, as well as for determining the content of macrocomponents in a sample and components with an average content.

– Cryoscopy (*measuring the amount of impurities in a base substance by means of measuring the temperature of crystallization*)—this method is mainly used in analyzing organic compounds.

– Isotope dilution mass spectrometry (*the method is, to a large degree, relative, since it implies the introduction of the so-called internal standard—an additive which can be a high-purity substance of the same element or its corresponding solution*). This method is applicable for analyzing inorganic and organic matrices in combination with additional methods (inductively coupled plasma mass spectrometry (ICP), gas chroma-

¹ In the original article, there were many translation errors. Here the article is reproduced in full with corrections.

tography - mass spectrometry, liquid chromatography - mass spectrometry).

Methods of comparison include also

- atomic-absorption spectroscopy;
- ICP atomic-emission spectroscopy;
- atomic-fluorescent spectroscopy;
- spectrophotometry;
- voltammetry;
- chromatography, etc.

To perform quantitative measurements, the above methods imply preliminary construction of a calibration graph.

In certification by preparation procedure, the traceability is ensured by using standard means for measuring mass (balances, measures of mass) that is on the list of base units of the SI system. The scheme of establishing the traceability of the results of measuring chemical composition to SI units, using certified reference materials (CRMs), is given in Fig. 1.

Under the scheme presented in Fig. 1, the size of the SI unit, reproduced by a measurement standard is transferred to the primary CRM by the primary method. Further, using the primary RM according to the measurement procedure (MP), based on the comparison method, the secondary CRM is certified.

Such a scheme to transfer the size of SI unit ensures the traceability in certifying a secondary CRM. From a secondary CRM, the size of SI unit is transferred by comparison method or that of indirect measurements to another CRM of composition or to the substances, analyzed to determine their component mass fraction.

The use of primary methods in CRM certification allows us to realize the direct traceability to the SI units.

One of the primary methods, namely, coulometric titration was taken as a basis of national standards and high-accuracy installations for determining the mass fraction of the base substance of chemical substances in many countries. Such installations (standards), based on the absolute method of coulometric titration, are successfully used in the United States, Germany, Slovakia, Japan, South Korea, China, Russia, and other countries.

In the period between 1976 and 1981, the Ural Research Institute for Metrology (FGUP "UNIIM"), created and certified high-accuracy installation (UVT) for reproducing the unit of base substance mass fraction in certified reference materials of chemical substances by coulometric titration, which was included in the State Register of UVTs (high-accuracy installations) of Russia under No. 14-A-81 (Fig. 2).

Six types of certified reference materials intended to reproduce and transfer the size of the unit of base substance mass fraction from the UVT to certified reference materials of a lower level and chemical reagents were developed on UVT 14-A-81. The list of CRMs

Fig. 1. Scheme for establishment of the traceability of measurement results for substance chemical composition to the SI units with the use of certified reference materials.

with indication of their metrological characteristics is given in the table below.

Reference materials of the first echelon, certified by coulometric titration on UVT 14-A-81 can be classified as primary reference materials.

The material of the indicated types of CRMs for composition can be obtained easily enough with a high degree of purity and is characterized by a high stability in time. The CRM data cover all types of chemical reactions realized in titrimetry: acid–base reactions, oxidation–reduction reactions, complex-formation reactions, and precipitation reactions.

CRMs for composition of potassium hydrogen phthalate and sodium carbonate ensure the uniformity of measurements of acid–base reactions, CRMs for composition of potassium bichromate and sodium oxalate cover oxidation–reduction reactions, CRM of the trilon B composition is used as a titrant in complex-formation reactions, and CRM of sodium chloride composition is applied in precipitation reactions.

The six developed and certified types of first-echelon CRMs for composition find broad application in the practice of analytical measurements:

- for establishing the titrated solution concentrations with a known error (uncertainty); in this case, the accuracy of quantitative chemical analysis (QCA) is the highest;
- for certification of lower-echelon CRMs;

Fig. 2. High-accuracy installation UVT 14-A-81 for reproducing the base substance mass fraction in certified reference materials for composition of chemical substances by coulometric titration.

Metrological characteristics of UVT 14-A-81

Range of measurements of base substance mass fraction, %	99.00–100.00
Type A evaluated uncertainty, uA , % ($n = 7$)	Not above 0.009
Type B evaluated uncertainty, uB , %	Not above 0.012
Combined standard uncertainty uc , %	Not above 0.015
Expanded uncertainty of CRM certified value U , % ($P = 0.95$)	Not above 0.030

– in realizing the scheme of within-laboratory and between-laboratory accuracy control of the QCA results;

– for evaluating the accuracy parameters of measurement procedures in their certification and use, etc.

The first-echelon CRMs of chemical substance composition can be also used in the quality control of works and for the assessment of the state of measurement in measuring and testing laboratories, during tests and certification of measurement instruments—analyzers of the composition of substances and materials, etc.

The traceability of the measurements of the unit of the base substance mass fraction is regulated by two normative documents:

– Recommendations on metrology MI 2639–2001 “GSI. State Traceability Chain for Instruments of Measuring Component Mass Fraction in Substances and Materials” [3];

– GOST R 8.600–2003 “GSI. Measurement Procedures for Base Substance Mass Fraction in Reagents and Highly Purified Substances by Titrimetric Methods: General Requirements” [4].

In accordance with the state traceability chain of MI 2639–2001, the unit of the base substance mass fraction is transferred from the six UVT-certified types of first-echelon CRMs to lower level CRMs for composition by comparison method, using a comparator or an indirect measurement method. For this purpose titrimetric

methods with a weight-dosed titrant are used. The error in the second-echelon CRM certification for the comparison method does not exceed 0.10%; for the indirect measurement method, 0.20%. The relative error of the third-echelon CRM certification by titrimetric methods, depending on the nature of the material and its aggregate state, may be 0.3–0.4% to 3.0% [3].

The State Standard GOST R 8.600–2003, developed for the establishment of this traceability chain, stipulates, depending on the accuracy requirements for the measurement of the base substance mass fraction (BSMF) of a reagent, the use of the following solutions as a titrant:

– based on the CRMs for composition of six chemical substances of the first echelon, covering all types of chemical reactions used in titrimetry (see table 1);

– prepared from CRMs for composition of chemical substances or CRM for composition of a solution of a titrant chemical substance;

– reagents in which the molar concentration of the equivalent of substance was established using CRMs for composition of chemical substances of the first echelon and CRMs for the composition of the corresponding substances [4].

A positive example of the establishment of traceability of measurement results for BSMF, using the first-echelon CRMs for composition, are the joint works between FGUP “UNIIM” and the Ural Plant of

The first-echelon certified reference materials (CRMs) for composition of chemical substances, certified by using UVT 14-A-81

Name of the first-echelon CRM for composition	CRM no.	Certified value for the base substance mass fraction, %	Expanded uncertainty of the CRM's certification (at $P = 0.95$), not above, %	Area of application in titrimetry
CRM for composition of potassium hydrogen phthalate	CRM 2216-81	99.90–100.00	0.03	Acidimetry
CRM for composition of sodium carbonate	CRM 4086-87	99.95–100.00	0.03	Alkalimetry
CRM for composition of potassium bichromate	CRM 2215-81	99.95–100.00	0.03	Oxidimetry
CRM for composition of sodium oxalate	CRM 3219-85	99.95–100.00	0.03	Reductometry
CRM for composition of trilon B (disodium salt of ethylenediaminetetraacetic acid)	CRM 2960-84	99.70–100.00	0.03	Complexonometry
CRM for composition of sodium chloride	CRM 4391-88	99.90–100.00	0.03	Sedimentometry

Chemical Reagents on producing a large nomenclature of CRMs for composition of ion solutions and upgrading a group of titration standard solution (the so-called standard titres) to the CRM category. The above works were run with observation of all the metrological requirements on the transfer of the value of BSMF unit from UVT through the first-echelon CRMs to CRMs for composition of ion solutions and to CRMs for composition of titrant solutions. To establish certified values of the CRMs, in accordance with the state traceability chain of transferring the value of BSMF unit, the first-echelon certified reference materials or titrants were used, in which the molar concentration of the equivalent (MCE) was determined using the first-echelon CRMs for composition of chemical substances. CRM certified values were established by titrimetric method according to MPs certified at FGUP "UNIIM" in compliance with the requirements of GOST R 8.563–96.

The measurement quality system in analytical chemistry rests upon the reference base and a large nomenclature of certified reference materials which also belong to the category of standards. Certified ref-

erence materials for composition of chemical substances play the most important role in the quality assurance of measurements in analytical chemistry—the use of primary certified reference materials (PCRMs), certified against a standard, and traceable secondary CRMs ensures establishment of traceability to the SI units, which in light of the current requirements for the results of measurements is one of the necessary conditions for their recognition by different countries of the world community.

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