

Certified Reference Materials of Geological and Environmental Objects: Problems and Solutions

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Abstract—A review of publications on the creation and application of certified reference materials for the chemical analysis of geological materials and environmental objects with the aim to ensure the uniformity of measurements is presented.

Keywords: certified reference material, geological materials, environmental objects, methods of elemental, isotopic, and substantial analysis

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Determination of the chemical composition of complex natural substances provides a basis for the majority of studies performed in Earth sciences (geology, geochemistry, oceanology, agrochemistry, etc.), and also in other fields of science and industry (environmental monitoring, exploration of mineral deposits, treatment of raw materials and wastes, building industry, etc.). Acquisition of such information requires substantial financial expenses. Statistically significant and comparable results of different analytical methods are necessary for the reliable characterization of the studied objects, for example, calculating values of geochemical “constants” (average abundance of elements in Earth’s crust, soil and other media [1, 2]; compositions of minerals, “petrochemical coefficients” [3–5]) or medicohygienic indexes (maximum permissible and approximate permissible concentrations, **MPC** and **APC** [6–10]), and also for the description of the directions of substance transfer in environmental media and technological processes [9–20], etc. The detection limits of analytes are changed due to the emergence of new and improvement of existing analytical methods, and in turn, the primary data used to calculate the standard values are also changed, that requires regular revision of MPC and APC to assess the state of the environment [2, 10, 16, 20–22]. Incomparable results obtained in different laboratories by different analytical methods substantially decrease the productivity of scientific research and industrial development.

Classifications of objects of analysis used in different branches of science considerably differ from each other. The glossary of terms [23, Article 3.9] characterizes the notion of “environment” as natural conditions and ecological status of a certain region. In this

case, the environment covers the whole natural environment (arose on the Earth independently of humans) and technogenic environment (i.e., environment created by humans). Natural and artificial (technogenic) environments include air, water, soil, natural resources, flora, fauna, humans, and their interactions [24]. In the last decades, geoecological studies [10, 20, etc.] and rapidly developing medical geology [25] follow this classification in studies of element and substance transfer between complementary media and in trophic and food chains, including rocks, water, bottom sediments, soils, plants, animals, and humans. According to [26], geological objects are different natural environments and those changed due to technogenesis, i.e., useful minerals (ore and nonmetallic mineral raw materials), rocks, loose and bottom sediments, soils, biological substances of plant origin, and surface and deep waters. According to the classification of objects accepted in Russian analytical chemistry [27] and used in this review, geological materials are only rocks and mineral raw materials and environmental objects are air, water, soils, and bottom sediments. The biota of plant and animal origin, inevitably reflecting compositions of the growing and living media (soils, water reservoirs) in this classification is included into the sections “Biological and Medical Objects” and “Food and Feed”. The assignment of an object of analysis to one or another classification is by no means conditional.

The complexity of the standardization of the analytical control of geological materials and environmental objects is due to the uncertainty of their typification. For example, because of the diversity of the complete chemical, substance, and structural compositions of granites [4, 5], widespread igneous rocks, the

development of a rational nomenclature of certified reference materials for their analysis was not successful [28]. In this connection, analysts in practice use cross-classifications accepted in different branches of science and industry [29–32].

A characteristic feature of the analysis of geological materials and environmental objects is often the necessity of the description of complete compositions, i.e., the necessity of the determination of major- and microcompositions, their isotope compositions, species, and composition of mineral phases both in unique samples of limited weight (nanophases of minerals, meteorites, Moon or Martian rocks, etc.) and in thousands of routine earth samples (exploration and geological prospecting works, environmental monitoring, or solving technological problems). Depending on the fundamental or applied problem to be solved, combinations of different methods and procedures applicable to studies of the whole diversity of both overall compositions of objects and concentrations of each target analyte at an economically justified ratio of the cost of analysis to the volume and quality of the obtained information are necessary. The used methods of elemental and substantial analysis are based on the different physical and chemical principles; each of them utilizes specific approaches and procedures in sample preparation to analytical procedures, measurements of analytical signals, and calibration of procedures. Analytical signals of each sample have individual noises caused by variations in the concentrations of matrix and interfering components.

Certified reference materials and their intention.

One of the means assuring the uniformity of measurements are certified reference materials (CRM) of the composition and properties [33]. Russian regulatory metrology defines certified reference material as samples of substance (material) with certified values of one or more property characterizing the composition or property of this substance (material) [33, article 2, p. 22]. CRM are intended for the following purposes [34, p. 5.1]:

—reproduction, storage, and transfer of property values characterizing the composition and properties of substances (materials), expressed in units accepted for use, also in tests and calibration of measurement, testing, analytical, and control equipment; in the certification and control of testing equipment and control of the accuracy of the results of tests using standardized procedures; for testing other certified reference materials; and in estimating metrological characteristics of measurement equipment in its testing and certification;

—demonstration of calibration and measuring possibilities;

—examination of the competence of test laboratories;

—interlaboratory comparative tests for the assessment of the applicability of unstandardized procedures.

The International Organization for Standardization (ISO) treats the problem of CRMs application in analytical chemistry [35–37] as the implementing of the chemical measurements for validation of methods (assessment of the suitability of the techniques for specific applications in a particular laboratory), traceability evaluating of the results and proficiency testing of laboratories. For these purposes researchers use the existing CRM and create new ones by validated procedures [38–49]. These are, first of all, multielement (matrix) CRM of different natural and technogenic environments (in different aggregation states) with having certified elemental, isotopic, and phase compositions. Such CRM are intended for the development of new methods (techniques) of analysis, except for the above tasks, and estimation of their detection limits. Producers of reference materials publish information on the types and compositions of numerous CRM of geological materials and environmental objects on websites and in international electronic databases (catalogues) [50–65].

From the scientific viewpoint, certified reference material is a tangible model of any substance, whose composition and properties were studied by specific algorithms and comprehensively described via certified property values. As any model, CRM must possess the property of stability (invariability of a substance within particular time interval) and completeness (the maximum characterization of the total mineral, elemental, isotopic, and particle size composition, and also the dimensions of individual phases). For any CRM, the consistency of information on certified property values documented according to [38–49] is understood as the ability of the known analytical methods (in their general population) to adequately reflect the actual situation, which is of principal importance, as it is based (in the absence of an alternative) only on the acceptance of the infallibility of the principles of analytical chemistry and in the validity of the law of large numbers [66].

In the SI system, the unit of measure of the amount of substance is mole [67–69]. Mole is used as a “unit” only in that sense in which truly mathematical scaling factors can be named units [70, 71]. Its use not fully assures the transition from the microworld of discrete objects (atoms and molecules) to the usual macroworld, in which kilogram (weight unit in the SI system) is considered a continuum, like length, time duration, etc. The problem will be solved when there appears a possibility of direct measurements of mass with errors smaller than the mass of some atoms (NIST-4 project).

The majority of up-to-date analytical methods are relative: analysts measure the value of an analytical signal, which is related to the amount of atoms or mol-

ecules to be determined (mass, volume, or atomic percent) by a certain functional dependence, rather than the number of atoms of an element or molecules of a compound. The universal approach to establishing a correlation between the measured chemical or physical property and the amount of an analyte—calibration—assumes the use of objects of analysis with the known characteristics of chemical composition, adequate to the analyzed samples in the analytical procedure [72, 73]. Thus, calibration is a particular type of mathematical simulation in analytical chemistry aimed at the account of the specific features of an object and their effects on the value and shape of the measured signal [74]. In this case, certified reference materials used for calibration are considered model objects.

The available CRM used in geoanalysis for calibration are usually incomplete models, because *numerical* information about their composition is provided not for all stable isotopes of the elements present and, the more so, their species and mineral phases. For example, *only* 50 elements were certified in the Russian CRM of the composition of the essexite gabbro rock (GSO 8670-2005) and information data were presented for concentrations of seven elements. For the CRM of quartz diorite, SKD-1 (GSO 6103-91), concentrations of 41 elements were certified and 20 elements were characterized as informative [50]. Certified data on the concentrations of 34 elements and isotope ratios of lead were provided in the certificate of the US CRM of the composition of andesite, AGV-2 [51]; in addition, informative values were provided for 16 elements. Usually CRM of ores are characterized mainly by non-numerical information: type of mineral raw material (sulfide, polymetallic ore, etc.) or its genesis (crust of weathering, mine refuses, etc.) and the minimum list of numerical metrological characteristics of only target (useful) and/or harmful impurity elements. For example, in the CRM of Brazil bauxites [52], concentrations of four mineral phases and eight elements were certified and approximate data on 10 elements were supplied; in the CRM of noble metals [75], concentrations of 1, 3, or 10 elements were certified.

Not only certified property values and accuracies of certified values, including characteristics of error (uncertainty) due to the method of certification and heterogeneity and instability of the CRM material, established for certified reference materials, but also other metrological and technical characteristics are important in analytical practice. They are determined at different steps of the CRM production, regulated by international and national normative and technical documents [39, 40, 42, 43, 48, 49]. Among these properties are estimating the homogeneity and minimum representative weights for the certified components; studying of time stability and determinations of the periods of validity of CRM materials; collecting and statistical processing of the obtained experimental

data for setting the values of certified characteristics and their errors (uncertainties); identifying metrological traceability; comparing new CRM with those developed earlier and similar in applicability. The results of tests and statistical processing are summarized in reports and specified in accompanying documents (type declaration, certificate, label) [41, 46], including the conditions of storage (also after opening packaging, if they are provided) and transportations, and recommendations for application.

The following stages of the development of CRM of geological materials and environmental objects cannot be unified: choice of candidate substances for CRM; procedures of the selection of necessary weight portions in natural or industrial conditions; substantiation of the use of particular methods of the preliminary study of mineral compositions and methods of elemental (isotopic) analysis; use of one or another technology of the disintegration of solid substances (crushing, grinding, homogenization) or methods of preservation (stabilization) of CRM of liquid and gaseous media; choice of measurement equipment for the description of particle size distribution in the powdered CRM. The composition of natural media changes in time and space because of permanent processes of substance redistribution, for example, the aerosol transfer of soil pollutants [76–78]. Thus, information about the place and time of sampling materials for CRM is not less important than the certified metrological characteristics.

History of problem origin of certified reference materials in geoanalysis. The problem of assuring the uniformity of measurements in the analysis of geological materials sharply arose only in the middle of the 20th century, because earlier intralaboratory reproducibility (precision) of the results was considered a quite sufficient characteristic of the quality of analytical methods. In comparing the results of analysis of granite, G-1, and diabase, W-1, the first certified reference materials of rocks developed by the United States Geological Survey, interlaboratory differences between the results of chemical analyses of samples were of the same order of magnitude as variations of the composition of similar, but petrographically different rocks [79, 80]. Interlaboratory comparisons of the results of analyses of other rocks, summarized in monographs [32, 66], showed that none of analytical methods can ensure the trueness of the results without tests of quality on natural CRM. The first CRM almost expired by the middle of the 1960s; therefore, the US Geological Survey started the development of six new CRM [81]. The absence of unified requirements hindered the development of CRM. Nevertheless, works on the creation of CRM of mineral substances were started in the USSR, DDR, Canada, France, Switzerland, Great Britain, and about 40 CRM of rocks were developed in the world by 1970 [32]. In the execution of the Canadian project on the certification of geological materials (Canadian Certi-

fied Reference Materials Project 1976–1982), 93 elements and compounds in 26 CRM of rocks and ores were certified by the data of an interlaboratory experiment [82]. More than 270 international CRM of the main silicate rocks and minerals were in use by 1989 [83]. The most complete summaries of the problems of the creation of CRM and systems of their use in 1950–1990 are presented in monographs [29, 31, 32, 66] and catalogues [84, 85].

The experience of the creation of CRM of substances and materials accumulated in the USSR and in the world practice was for the first time formulated in the Soviet Union and as *GOST* (State Standard) 14263-69 “General Requirements to Reference Materials of Substances and Materials” [86]. The document favored the expansion of the activity of different organizations in the spheres of applied and theoretical metrology, supervised by Gosstandart of the USSR and specified a complex of tasks on the study, selection, and preparation of materials, assessment of uniformity, design of interlaboratory experiments, and statistical data processing [87–89]. Similar documents on CRM were developed in 1971–1974 by the countries members of the Council for Mutual Economic Assistance [90]. The results of studies in the spheres of theoretical (including nonparametric statistics) and applied metrology allowed the creation of a seamless system of regulatory metrology in the USSR by 1980 based on State and Branch Standards for the standardization and quality control of analytical works in the Ministries of Geology, Ferrous and Nonferrous Metallurgy, Medium Machine-Building Industry, Hydro-meteorological Service, etc.

In the International Organization for Standardization, similar works were started a little later. REMCO (Committee on Reference Materials), a special committee of the Council of ISO was organized in 1975 [91] for the development of corresponding guidelines on problems dealing with certified reference materials (standards) and interaction with international metrological organizations, in particular with the International Organization of Legal Metrology, IOLM. Guidelines *International Vocabulary of Metrology: Basic and General Concepts and Associated Terms*, *Reference Materials: Selected Terms and Definitions*, *Reference Materials: Contents of Certificates, Labels, and Accompanying Documentation*, *Reference Materials: Good Practice in Using Reference Materials*, and *Certification of Reference Materials: General and Statistical Principles* were developed ten years later (1982–1985). Updated versions of these documents appear after regular revisions and actualization [44–49].

Before Russia joined the World Trade Organization, international metrological institutes put forward the necessary condition of changing to ISO requirements in the production of goods and services, liquidation of fundamental and terminological differences legislated in the state and branch standards, and can-

cellation of national normative documents or their harmonization with ISO documents [92, 93].

Information support of geoanalysis. *Geostandards Newsletter* (present name *Geostandards and Geoanalytical Research*), an official journal of the International Association of Geoanalysts (IAG) is published starting from 1977 [94] with the aim to inform the geological community about works on the creation of certified reference materials for geoanalysis. Today the main tasks of the International Association of Geoanalysts consist in the progression of geoinformation and analytical sciences (i.e., geoinformation systems utilizing data of chemical analytical methods for the generation of different maps), support of studies in new methods of selection and analysis of geological and ecological samples, improvement of the system of assessment of the uncertainty of measurements and data quality by professional testing of laboratories, and compilation and use of information materials. Starting from 1979, the journal publishes annual reviews of publications in English journals on the achievements, problems, and methods of their solution in the field of certified reference materials, for example [95–102]. Russian journals translated into English are not covered by in these reviews. A list of journals regularly discussing problems of the creation and use of CRM of geological materials is presented in the table. In the last decade, the list of English journals changed a little, but the list of Russian journals is expanded. In Russian literature, information about Russian and foreign CRM for geoanalysis is considered in different journals, but is not generalized for users, because it is not clearly structured and only partially falls within the scope of obligatory governmental control [33], in spite of the fact that CRM of geological materials and environmental objects are used for the calibration and verification of spectral instruments. Thus, according to the data [29, 93], CRM of geological materials appear in categories of CRM for ferrous and nonferrous metallurgy, environmental monitoring and environmental protection, agrochemistry, building and construction and power industry, safety of food and agricultural products, high-purity materials, etc.

The figure illustrates the dynamics of publishing articles on the creation and application of CRM in Russian journals in the last 13 years by the data of the scientific electronic library eLIBRARY.RU [103]. Except for the journals listed in the table, we also considered the journals *Standarty i Kachestvo*, *Mir Izmerenii*, *Zakonodatel'naya i Prikladnaya Metrologiya*, *Karotazhnik*, etc. Note that 90% of articles published in 2008–2010 were devoted to the explanation of the use of the Federal Law “Assurance of the Uniformity of Measurements” [33]. Starting from 2005, specialized journal *Standartnye Obrazttsy* is the leading journal in the problems regulatory, theoretical, and applied metrology in Russia, including publications on the development and application of CRM. Problems of the standardization and certifica-

English and Russian scientific journals, regularly publishing information on the development, investigation, and application of certified reference materials for the chemical analysis of geological materials and environmental objects

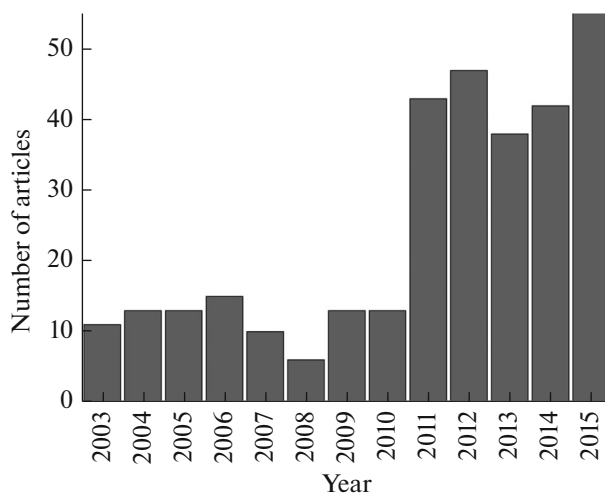
Journals in English [95–102]	Journals in Russian [103]
Analytical and Bioanalytical Chemistry	Analitika
Analytica Chimica Acta	Analitika i Kontrol'
Applied Geochemistry	Vestniki Vuzov*
Chemical Geology	Woda: Khimiya i Ekologiya
Contributions to Mineralogy and Petrology	Geologiya i Geofizika
Earth and Planetary Science Letters	Geokhimiya
Environmental Research	Estestvennye i Tekhnicheskie Nauki
Geochemistry Geophysics Geosystems	Zhurnal Analiticheskoi Khimii
Geochimica et Cosmochimica Acta	Zhurnal Prikladnoi Spektroskopii
Geostandards and Geoanalytical Research	Zavodskaya Laboratoriya. Diagnostika Materialov
International Journal of Mass Spectrometry	Izvestiya Akademii Nauk. Seriya Khimicheskaya
Journal of Analytical Atomic Spectrometry	Izmeritel'naya Tekhnika
Journal of Petrology	Kontrol' Kachestva Produktsii
Journal of Radioanalytical and Nuclear Chemistry	Neorganicheskie Materialy
Lithos	Obogashchenie Rud
Microchimica Acta	Poverkhnost'. Rentgenovskie, Sinkhrotronnye i Neitronnye Issledovaniya
Precambrian Research	Radiokhimiya
Science of the Total Environment	Razvedka i Okhrana Nedr
Spectrochimica Acta Part B	Standartnye Obraztsy
Talanta	Ekologicheskie Sistemy i Pribory

* Integrated news of higher educational institutions and bulletins of state universities.

tion of materials and accreditation of laboratories are also discussed in the journal *Zavodskaya Laboratoriya. Diagnostika Materialov*. The less important role of the *Journal of Analytical Chemistry* in the rating is explained by the fact that the search in the eLIBRARY.RU system was performed by the attribute "certified reference material," which is usually not present in the keywords of articles published in this journal.

Articles in foreign and Russian journals containing CRM data are close in subjects. They discuss the assessment of the analytical possibilities of methods using CRM, comparison of different methods by the results of analysis of CRM, development of new types of CRM, expansion of the list of established metrological characteristics in the already known CRM, development of statistical approaches to the collection and processing of experimental data for CRM, and the available and developed standard documentation.

Methods of analysis and CRM of geological materials and environmental objects. Problems of the development and application of CRM are associated with



Distribution of the number of articles on the development, investigation, and application of certified reference materials for the chemical analysis of geological materials and environmental samples in Russian journals according to electronic library e-LIBRARY [103].

two aspects of the analysis of samples varied in composition and the state of aggregation. The first aspect is the development of methods of geoanalysis for the determination of total concentrations and isotopic compositions of elements, speciation (presence) of elements (or compositions of mineral phases), and their sizes. For all analytical methods (direct, indirect, hybrid), CRM are necessary for assuring accuracy in the optimization of procedures, such as sample preparation and the transfer of analytes into species convenient for measurements; calibration; and estimation of the limits of detection and precision of the results of different analytical methods. The second aspect is the account of features (specifics) of the objects of analysis (variability of mineral phases and element speciation, representativity of weighed portions, level of analyte quantification) on the assumption that the stages of CRM development correspond to the permanently updated requirements of standard documents, including methodological approaches to the accumulation of analytical data and statistical algorithms for their processing.

Earlier, Ministry of Geology of the USSR [31] and US Geological Survey [104] recommended the use of a wide range of analytical methods for the study of geological materials. In the last 10–15 years, considerable changes associated with the development and computerization of analytical instruments and their mass use in routine analyses occurred in analytical laboratories involved into geological and ecological studies [105]. Physicochemical methods have become prevailing, and **monoelement** methods (techniques) were replaced by **multielement** and group methods [106–119]. At the same time, for a number of elements (halogens, alkali and precious metals), the existing monoelement procedures is some cases could not be replaced. This is particularly true for methods, such as electrochemistry [120], spectrophotometry [112, 121, 122], atomic absorption spectrometry [123, 124], and fire assay [125, 126].

The expansion of the possibilities of methods, both direct and involving preliminary transfer of samples into solutions, attained through the improvement of the analytical equipment and software, was shown on results of the analysis of CRM. Publications regularly cover the use of CRM in the analysis of new sources of excitation of atoms and ion formation, detectors, equipment for sample preparation, and/or methodological approaches to the account of specific features of particular objects (water, sediments, rocks, ore and nonmetallic raw materials, soils, etc.). Examples are presented in reviews and original articles: X-ray fluorescence analysis (XRFA) [127–130], neutron activation analysis (NAA) [131, 132], atomic emission spectrometry (AES) [133–141], atomic absorption spectrometry (AAS) [123, 124, 142–144], mass spectrometry (MS) [145–152], etc. Problems of the application of CRM were also considered for local methods of analysis, focused on the determination of

concentrations of a wide range of elements, composition and sizes of mineral phases, and isotope ratios in single mineral micrograins, i.e., electron probe microanalysis (EPMA) [153–156], laser-induced breakdown spectroscopy (LIBS) [157, 158], and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [154, 156, 159–161].

Among the important advantages of geoanalysis are the significant reduction of the detection limits for elements, expansion of the range of simultaneously determined elements, and improvement of methodological procedures (method of standard additions, method of external and/or internal standard, isotope dilution, ion exchange, adsorption preconcentration, etc.) [162–168], ensuring the analysis of diverse objects by one procedure [133, 141, 169] at an improved accuracy of the results and an increased throughput. The majority of state-of-the art methods operate with sample portions smaller than 0.1 g, which makes the **estimation of particle size distribution and the degree of uniformity** of element distribution in powdered CRM quite important for the newly developed CRM [153, 170–172].

Note that CRM of natural media and those changed in processes of technogenesis are multicomponent substances with complex organo–mineral compositions. Their milling gives particles of different specific weights, differing in volume and shape [32, 173–175]. Variations in the particle size distribution of powders are, first of all, due to the simultaneous presence of mineral phases with hardness in the Mohs scale varied from 1 (coal) to 8 (quartz), hindering grinding to equally fine particles, especially for small amounts of minerals with high hardness. The certified elements are quite often presented by **several mineral phases**, each of which is characterized by individual distribution and fraction in the substance bulk. Estimation of uniformity, its contribution to the error of the certified value, and determination of the minimum representativity by weight should be performed by analyzing weighed portions of CRM of different weights [39, 42, 48]. If such experiment cannot be performed for the whole range of certified elements wither for economic reasons or because of the unavailability of a corresponding analytical method for the developers, values of uniformity found for indicator elements are prescribed to such elements [39, 42]. The choice of an indicator element requires additional studies of the substance composition of the CRM (i.e., financial expenses); otherwise the estimate of uncertainty due to the heterogeneity of element distribution can be incorrect.

As was noted above, a great number of multielement powder CRM of different geological materials were developed before 1995. They were **certified** mainly by the results obtained by **mono-element chemical methods of analysis** (gravimetry, titrimetry, spectrophotometry, polarography, atomic emission and

atomic absorption spectrometry with preliminary adsorption and extraction of analytes, etc.) [32, 66]. Microelemental composition was determined using chemical separation and preconcentration. The error introduced by these procedures into results of analysis is greater than the error of spectral measurements of analytical signals on present-day instruments [176]. Therefore, the mean values for the majority of rock-forming elements were obtained by the vast majority of data of these methods of chemical analysis, involving the obligatory transfer of the solid substance (powder) into a solution and operating with a priori representative weights from 0.2 g to several grams. Such weighed portions were analyzed in the determination of microelements by procedures involving preliminary extraction and adsorption. In certificates of CRM, representative weights for the determination of gold were set based mainly on the results of fire assay and equaled 25 and 50 g.

By now, various devices have been developed for transferring powder samples into solution. They ensure the intensification of the process in vessels of normal and elevated pressure on thermal heating and under the application of ultrasonic and microwave fields [177]. In acid digestion in microwave systems, the optimum weighed portion for the determination of macroelements was set at 0.1 g and, in some cases of the determination of microelements, 0.05 g [178]. As was confirmed experimentally, the representative weighed portion of the available CRM can be reduced to 30 mg without the deterioration of the precision of the results of determination of rock-forming, rare-earth elements, and platinum-group metals by ICP-MS [179] and synchrotron radiation XRFA (XRFA-SR) [180]; in arc discharge AES procedures, the portion may be 5–10 mg [181, 182]. For local methods, the analyzed weighed portions are smaller than 0.001 mg [172]; therefore, the requirements to the uniformity and particle sizes of calibration CRM and samples become even more stringent.

Powder CRM can segregate on storage, and their homogenization is a very complicated procedure [32, 171]. Longer disintegration quite often leads to losses of analytes in mechanochemical reactions [183], an increase in particle size due to agglomeration, and also to changes in the composition of mineral phases [184, 185] rather than to the reduction of particle sizes. For CRM from the collection of the Institute of Geochemistry of the Siberian Branch of the Russian Academy of Sciences, the refined descriptions of particle size distribution obtained on a HELOS laser diffraction analyzer (Sympatec GmbH) in the dry dispersion mode point to the constancy of the particle size of powder CRM of bottom sediments (BIL-1, BIL-2), metamorphic rocks (SChS-1, SLg-1), and ashes of coals (ZUK-1, ZUA-1, ZUK-2) and to the stability of substances prepared more than 40 years ago [174, 175]. It was shown that, for the majority of the certified elements, **the new representative weights** calculated by the

data of direct AES with arc discharge [176] were 0.05–0.1 g, while those provided in certificates appeared smaller [174–176]. The estimates obtained agree with the data of AAS and ICP-MS analyses of 0.2- to 2-g weighed portions of CRM samples of BIL-1, SChT-3, SDPS-2, SChS-1, and SLg-1 [144, 145]. As powder CRM containing nanodimensional mineral phases are widely used in geoanalysis, the application of procedures of the assessment of the homogeneity of nanomaterials [186, 187] seems advisable in the development of some CRM.

Certified reference materials in calibration tasks.

Theoretical and applied calibration problems were discussed in IUPAC official reports [72, 73], Russian State Standard [74], and numerous publications on particular analytical procedures. The analyst in calibration must find the law of transformation of the input chemical signal into the output analytical signal $I = F(c)$, where I is the measured analytical signal, c is element concentration in the sample, and F is a certain transformation function. The measured values reflect the multifeature nature of real samples and processes, occurring in the formation and measurement of an analytical signal [188, 189]. Interferences introduced into the measured signals because of changes in macrocomposition and the effects of interferents are individual for each particular sample. For example, researchers detected a significant effect of water on the intensity of lead lines in LIBS [190]; lines of iron, uranium, zirconium in time-of-flight MS with pulse glow discharge ionization [191], and in the IR determination of carbon, hydrogen, nitrogen, and sulfur [192]. The accuracy of the determination of age in using CRM of zircon in geochronology is also affected by the main matrix component [193]. Nevertheless, optimization of methods for the calculation of analytical signals ensures the account of nonspectral effects in AAS with continuous excitation sources [194] and in AES using a plasmatron and an arc source [141, 188]; this allows the researcher to use bi-logarithmic linear calibrations.

Calibration samples comparable to the studied samples in composition for the determination and regular validation of constraint equations for the maximum account of matrix effects and spectral overlaps are required in the calibration of spectral methods of analysis of solid and powdered samples, such as XRFA, XRFA-SR, EPMA, secondary ion mass spectrometry (SIMS), LA-ICP-AES, arc discharge AES, LIBS, LA-ICP-MS, etc. The so-called standardless methods of analysis imply calibration by the spectra of CRM of pure substances or certified mixtures [195–197] at least at the initial stage. A possibility of the determination of the amount of substance by theoretical spectra and the instrument function of the spectrometer was shown in [198]. The main difficulty of this approach is the compilation of a spectral library for each substance and each instrument based on spectra of real substances.

The recent trend demonstrates that the use of multidimensional approaches to calibration for the revelation of hidden regularities, representing the most significant characteristics of an object in a multidimensional space, is most preferable [73, 133, 199, 200]. Variations of factors affecting signal intensity are corrected by the type of calibration and careful selection of a training set of calibration samples, in some cases inadequate to the composition of the analyzed materials [200–206]. In this case, matrix and spectral effects are reduced, the analytical range for using one and the same procedure is extended, and/or the accuracy of the results of analysis is improved. Diverse matrix CRM are used for the confirmation of the extension of analytical ranges in procedures with classical linear calibration models [135, 152, 207] and the reduction of the actual limits of detection in analytical procedures involving multidimensional calibration [203, 208–211]. In the last case, sets of CRM with different matrix compositions and certified concentrations of analytes near their limits of detection must be available. The list of such CRM is insufficient for the calibration of highly sensitive methods and procedures. The determination of certified concentrations and their uncertainties by procedures with the limits of detection differing by several orders of magnitude seems problematic [212].

This is a reason for which standard solutions of ions, also presented in CRM sets, are widely used as calibration samples in geoanalysis [54–65]. However, CRM of surface and deep natural waters were used only for the quality control of the results [138, 149, 150]. The number CRM of natural waters and atmospheric precipitates is limited; they are unstable on long storage and transportation [213–220]; therefore, simulators of natural substances, mixtures of salts dissolved under specified conditions [216] or substrates on filters and resins bearing preconcentrated analytes [218–221], are widely used in the analysis of similar samples.

Problems of the determination of high and low concentrations [2, 185] arise regardless of the method and object of analysis, especially for CRM of complex mixtures and pure substances [222–224]. They are associated with the low accuracy of the determination of impurity element concentrations close to limits of detection and also at high concentrations of the major substance in inorganic and organic substances [225–227] and/or analytes in complex mixtures of organic and mineral substances [224, 227].

New data for CRM and new CRM. Original articles usually contain data of different analytical methods on the compositions of certified reference materials used for calibration, validation of procedures, and quality control of the results of geoanalysis. New data obtained for previously developed powder CRM in the determination of elements playing an important role in geochemistry and ecology allowed us to compare

the results for one or several components obtained using different methods of analysis and sample preparation, and to find the optimum conditions of their application. For example, for Russian and foreign matrix CRM of rocks, sediments, and soils, new data were published on rare-earth elements in the highest oxidation states [145, 146, 179, 228–231], gold and platinum-group metals [139, 145, 147, 152, 168], and toxic elements [144, 232, 233]. The producers of CRM use this information for the confirmation of the stability of substances; extension of the list of substances with prescribed metrological characteristics; and refinement of earlier certified concentrations of elements and their uncertainties. For example, for referent materials of the Geological Survey of Japan, which had no metrological characteristics before, certified concentrations were prescribed by the data published in the last 20 years. These concentrations are presented in the GeoRem database [102].

Present-day technologies ensure the extraction of a great number of useful components from crude ores, also containing elements in low concentrations. Therefore, **previously developed CRM** of rocks and ores are **recertified**. This is typical for the major producers and distributors of CRM, such as the US National Institute of Standards and Technology (NIST), US Geological Survey (USGS), Canada Geological Survey (CGS), Japan Geological Survey (JGS), Mongolia Geological Survey (MGS), etc. [102]. Thus, in the recertification of CNRC MP-2-83 (tungsten–molybdenum ore [82]) in 2012, the number of certified elements was increased from 5 to 35 and the previously specified property values were refined [234].

Both earlier developed natural zircon materials 91500 [235] and new samples GJ-1 [236] are widely used for geochronological measurements; data for these CRM are published together. New CRM were developed for the *in situ* determination of lithium isotopes by SIMS and LA-ICP-MS [237]. Information about the creation of new CRM producers in Russia is published in the journal *Standartnye Obraztsy*, and data on CRM of foreign production, in *Geostandards and Geoanalytical Research* and are included into the GeoRem database [60].

The publications discuss **approaches to methods of CRM preparation**. For microanalytical studies, analysts recommend preparation of tablets from pressed powders of nanoparticles and/or natural materials [238, 239] and also vitrification methods, because of the absence of CRM for different matrixes for EPMA and LA-MS [161, 240, 241].

Assurance of **traceability** [214, 242–244] is also an important feature of measurements used to study changes in the environment, because they are aimed at the detection of small changes within wide time intervals and must use certified reference materials stable within dozens and hundreds of years [174, 185, 245].

CRM must be consistent within national collections, and collections from different producers must be consistent between themselves [185, 246–248]. However, for multielement matrix CRM, the recommended methods of comparison and estimation of consistency are insufficiently well theoretically substantiated.

The regularly published reports on the **execution of global/regional geochemical projects and compiled atlases of the distribution of elements** in different territories, discuss the creation of CRM collections ensuring the standardization of conditions of gaining analytical information for the estimation of background values, MPC, and APC of elements [11–15, 249, 250]. It is known that the bioavailability of elements present in different chemical compounds (species) differently affects the growth of plants and living organisms [9, 10, 18, 20–22]. In this regard, the execution of projects on the study of the composition of forest soils [76], soils of agricultural lands, and their productivity [25] ensures the assessment of the speciation (water-soluble, acid-soluble, mobile, carbonate, etc.) of essential and toxic elements [78, 208, 251–257] and the determination of isotope compositions [258–260]. The development of CRM of soils with certified concentrations of species of different bioavailability is a very difficult task, because procedures of the extraction of individual element species or their groups from various soils are insufficiently unified. In this situation, the data sets are non-uniform and the assessment of the mean value and its uncertainty seems problematic [77, 78].

The number of **CRM of elements species** developed by now is quite insufficient; geochemical multielement standards of associated media, for example, CRM of water – CRM of hydrobionts – CRM of water plants – CRM of bottom sediments; CRM of rocks – CRM of loose deposits – CRM of soils – CRM of terrestrial plants – air are also virtually absent. The progress of medical geology [25, 224] in the development of new CRM requires focusing of efforts on the certification of low levels of total concentrations and species and isotope compositions of elements and organic compounds. Great attention in the performance of such measurements is given to hybrid procedures of analysis with preliminary separation and/or preconcentration of individual species, such as capillary electrophoresis [118], chromatographic separation [119, 254], ion exchange [167], solid-phase extraction [255], and flotation [182].

A promising line is in the simultaneous application of several analytical methods, for example, isotopic and atomic emission analysis. In [261], isotopic analysis was used to determine ^{210}Pb with the aim to calculate the rate of formation of bottom sediments and the amounts of accumulated pollutants (Cu, Pb, Zn, Cr, Ba, Mn, Al, Fe) within the corresponding time; their gross concentrations were found by an ICP-AES procedure.

The determination of the composition of mineral phases in CRM of powdered geological objects remains a complex challenge, though gross concentrations and element speciation in powders can be simultaneously determined by XRFA [262]. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio (indicator for the classification of the conditions of rock formation) is not always satisfactorily reproduced in the analysis encoded of CRM by titrimetric, spectrophotometric, and X-ray fluorescence procedures [230].

The possibility of the determination of the composition and size of mineral phases was shown for LIBS [157] and EPMA [153, 184]; their identification with particular deposits was described in [263, 264]. A methodological approach to the development of five new CRM of phase composition for technological products of gold-extracting factories was proposed in [265] using quantitative X-ray powder diffraction.

Methods and tools for the creation of multiparameter CRM of composition and properties were discussed in [266–268]. Multiparameter CRM with certified values of the composition of mineral phases, their size, and amount of any phase are necessary in analytical methods simultaneously measuring these characteristics of geological objects: automated mineralogy based on standardless EPMA methods [269] and scintillation atomic absorption [270] and atomic emission spectrometry [204, 271]. For radioactive CRM with isotope compositions changing in time, producers provide time dependences as certified characteristics and errors of the certified values take into account the error of the half-life period [272]. In the Russian nuclear industry, a new notion of “certified object” [272] was introduced and is used now in addition to traditional CRM, also for radioactive ores and environmental objects. In this approach, immaterial objects that do not meet the definition presented in the Federal Law [33] can be used as analogs of certified reference materials. Such samples are images of microstructure objects (files rather than material images), for example, images of the grain structure of uranium dioxide tablets, for which qualified experts characterized grain sizes by expert estimates. Such an approach is promising for methods using image analysis of geomaterials, for example, EPMA, LIBS, and automated mineralogy.

Validation of analytical procedures, professional testing of laboratories, and certification of CRM. Methods of elemental and substance analysis used in present-day geoanalysis are based on different physical and chemical principles; therefore, everyone follows specific approaches and methodological procedures in sample preparation to analytical measurements and calibration of procedures. To refine of the analytical possibilities of procedures, procedures are validated; to confirm the competence of laboratories, professional testing of laboratories is performed according to recommendations [273–276]. In carrying

out these procedures with the aim to ensure the traceability of results, one should use different CRM, preferably matrix ones, with the widest ranges of analyte and interferent concentrations [275–277]. The advantages of this approach are evident, because in the use of CRM, the certified value, its uncertainty, and traceability are independent of the results of measurements if matrices of the CRM and analyzed object are comparable. However, economically available CRM with natural matrices for continuous use in qualification test programs are often absent. In this case, it was proposed to certify the material of big sample lots by the results of measurements using a calibration dependence based certified values for a set of CRM with comparable matrices [275]. If CRM with similar matrices are absent, it was proposed to prepare synthetic test samples gravimetrically, by adding pure substances or certified CRM with less suitable matrices [278, 279]. Then the calculated mean value can be traced to the concentration certified in the CRM and to the kilogram standard. Programs of interlaboratory comparison tests of the assessment of professional qualification according to the above approaches are executed by national branch [279] or international [94, 224, 278] organizations. Restrictions on use of measurements for not certified samples and the incorrectness of estimates in the execution of professional test programs for not certified reference materials were discussed in [280, 281].

The International Association of Geoanalysts fulfills Program (I) GeoPT aimed at the professional testing of laboratories analyzing natural and synthetic geomaterials starting from 1996 and Program (II) GeoPT G-probe for microanalysis starting from 2008 [94]. The special IAG committee is engaged in the certification of CRM by the data obtained in the programs [282]. They analyze both not certified materials and certified reference materials. Laboratories present the results obtained using only routine measurement procedures, mainly XRFA (macroelements) and ICP-MS (microelements). The certification of CRM according to ISO Guidelines [47–49] fundamentally differs from the requirements of the GeoPT program of professional testing in the procedures of data acquisition [282] and processing for the determination of the mean value and its uncertainty, which are based on semiempirical algorithms [283] proposed for the assessment of the quality of the results of analysis of food and do not taking into account the natural specificity of geomaterials. It is likely that just for these reasons, concentrations of a number of elements in CRM certified previously according to guidelines [47–49] do not coincide with the prescribed average concentrations calculated according to the GeoPT program or do not allow their establishment for the earlier certified elements [284, 285].

The analysis of silicate rocks [286] in the GeoPT program (21 round with the number of participating laboratories 68–88 was performed in 2001–2010)

showed that the determination only of 22 elements (Si, Al, Mn, Cs, Dy, Er, Eu, Ga, Hf, Ho, Lu, Nd, Pr, Sm, Sr, Tb, Tl, Tm, U, Y, Yb, Zn) was satisfactory in the whole range from average abundance of elements in Earth's crust to ore concentrations; 24 elements (Ti, Fe_{total}, Mg, Ca, Na, K, P, Ba, Be, Cd, Ce, Co, Gd, La, Li, Nb, Rb, Sb, Sc, Sn, Ta, Th, V, Zr) were well determined in average concentrations ranges and demonstrated unsatisfactory results at low/high concentrations; the results of determination of nine elements (As, Bi, Cr, Cu, Ge, Mo, Ni, Pb, W) and their losses after calcination were unsatisfactory in the whole range of analyzed concentrations; and concentrations of 23 elements and three components could not be determined in routine analyses (Ag, Au, B, Br, Cl, F, Hg, I, In, Ir, N, Os, Pd, Pt, Re, Rh, Ru, S, Se, Te, Fe²⁺, H₂O⁺, CO₂). In addition, significant systematic errors in the results of ICP-MS determination of Zr, Y, and rare-earth elements using routine acid digestion procedures were revealed for some silicate rocks [284]. If such results were used for certification, the reliability of CRM was doubtful; therefore, organizers discussed the need in the modification of professional testing procedures GeoPT (I) on the collection and presentation of measurements [287].

The current paradigm of geoanalysis, promoted by the International Association of Geoanalysts [94] and the companies manufacturing analytical equipment, according to which two methods of multielement analysis (XRFA for the determination of major elements and ICP-MS for the determination of microelements) and microprobe analysis (transmission electron and X-ray scanning microscopy) to be sufficient for gaining analytical information about geological samples and studying their substantial composition, has to be revised. The appropriateness of using AAS and ICP-AES or NAA is some specific tasks is recognized. However, atomic emission spectrometry, spectrophotometry, electrochemical methods, etc. are considered as methods of reanalysis, increasing the cost of geoanalytical works. This restriction does not seem reasonable, because today the levels of automation and computerization of all methods are close to each other, but XRFA and ICP-MS procedures cannot be calibrated and validated in the absence of CRM of geological materials similar to test samples [277, 278, 284, 285]. The proposed reduction of the cost of the determination of elemental compositions cannot compensate the unreliability of information obtained by only two methods.

In the interlaboratory certification of CRM, the method must be included into the research list according to its analytical possibilities, restrictions, and advantages, such as real improvement of rapidity, limits of detection, precision, and, which is most important, accuracy of the results of analysis with regard to its simplicity and economic feasibility [31, 66, 281]. Professional test programs must be based on the use of

reference materials with prescribed reference values for analytes.

Provision of geoanalysis with certified reference materials. As was noted above, the widest variety of analyzed geological media creates insurmountable difficulties in their unification aimed at the development of a universal nomenclature of CRM. The creation of an optimum system of certified reference materials, universal for the whole variety of geoanalytical tasks, today is also impossible. In this regard, provision with certified reference materials should be considered depending on particular analytical tasks (method and object) and areas of their application (calibration or validation of procedures, assessment of qualification).

For the last 60 years since the appearance of the problem of the uniformity of measurements in geoanalysis, the number of CRM of natural objects in Russia increased by 2–3 orders of magnitude (crude ores and nonmetallic raw materials, soils, sediments, slits, waters, etc.). However, their percentage in the total number of CRM types today does not exceed 10% [29, 92] and incompletely satisfies the requirements of scientific and industrial laboratories [93]. Analytical works in the study of the substance and isotopic composition of geological materials are insufficiently well supplied with certified reference materials, because of growing the number of analyzed water and soil samples, slits, and sediments, in which bioavailable compounds and species of elements and their isotopes are determined. Up-to-date direct instrumental analytical methods (EPMA, scintillation AES, etc.) for the study of the composition of crude ores and nonmetallic raw materials and comparison of enrichment technologies are not supplied with multiparameter CRM for calibration and control of the accuracy of the results. The application of multicomponent CRM, including 50 and more indicators as certified values, ensures an actual increase in rapidity, efficiency, and economic appeal of analytical works.

It should be remembered that works in the field of geological CRM should also meet general requirements of the systems of international and national regulatory metrology, and their basic documents exhibit fundamental differences. In Russian Federation, the State Service of Standard Specimens for ensuring the uniformity of measurements forms the Federal Information Fund [53] and generalizes and harmonizes activity on the development, testing, and introduction of CRM [92, 93] with international documents. Based on the database of CRM of the composition and properties of substances and materials, issued in the Russian Federation, an automated information-analytical system is developed, which will help in the quick revelation of contradictions in normative documents of different levels, search for CRM of the necessary nomenclature, govern management decision making on the reduction of expenses in the recertification of the existing CRM and the creation of new CRM for

their efficient application to new technologies [288]. The full simultaneous reversion of Russia to the international practice of the development, certification, and approval of CRM is impossible without taking into account the advanced development of theoretical and regulatory metrology in the USSR before 1990. It will necessitate the revision of technical documentation for the produced CRM by 98% and destroy the national independence of the Russian Federation in assuring the uniformity of measurements. In this connection, the establishment of a new Russian program of the recertification of the earlier certified CRM of natural and man-made media is required; it will minimize losses in the harmonization of international documents and legal acts.

* * *

The importance of multielement matrix CRM of natural and technogenic media in chemical analysis is high and cannot be overestimated in ensuring the uniformity of measurements, gaining reliable information and new knowledge about the surrounding world, and reasonable decision making. Present-day mono- and multielement analytical methods use certified reference materials with the aim to reduce the limits of detection in routine measurements; estimate the possibility of the account of matrix effects and spectral noises in calibration. The application of CRM provides both calibration and wide measurement possibilities of various methods and procedures of chemical analysis; the development of new analytical methods and the certification of analytical procedures; their selection or combination aimed at the achievement of the best and economically feasible result. Because of the improvement of analytical methods, studies of the stability of CRM substances, assessment of the homogeneity of element distribution, description of particle size distribution, and determination of the minimum representative weights could rise to a new level; there are possibilities of the expansion and specification of the list of certified characteristics. To improve the efficiency of the application of the available CRM, determine the most important quality criteria in the certification of CRM for different tasks and methods of analysis, to which one should approach in the recertification and creation of new CRM, we should join together efforts of experts in analytical chemistry and consumers of analytical data, geologists, geochemists, mineralogists, ecologists, metallurgists, technologists, etc., and, of course, metrologists.

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