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PRACTITIONER'S REPORT

Certification of reference materials for inorganic trace analysis: the INCT approach

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Abstract This paper presents the work done by the Institute of Nuclear Chemistry and Technology (INCT), Warsaw on a procedure of the certification of matrix reference materials (CRMs) for inorganic trace analysis. The INCT has been involved in preparation and certification of that type of CRMs since 1986 till now. The certification of CRMs is performed on the basis of statistical evaluation of the data obtained from the worldwide interlaboratory comparison. The initially adopted certification procedure has been developed, and the final shape is presented and discussed. The modifications are connected with the new demands of the international standards. The results of analysis of candidate CRMs obtained by the potentially primary procedures based on radiochemical neutron activation analysis (RNAA) and results of analysis of CRM accompanying candidate RMs are applied in the certification process for quality assurance purpose.

Keywords CRM · Certification · Radiochemical neutron activation analysis · RNAA primary procedure · Traceability

Introduction

Certified reference materials (CRMs) are a significant part of quality assurance in analytical chemistry [1–3]. CRMs play a similar role in chemical measurements like reference standards in physical ones. So, they should establish metrological traceability when are applied for calibration of chemical measurement process or comparability of the results when used for quality assurance purposes [3–6]. The INCT has been involved in the preparation and certification of CRMs for inorganic trace analysis since 1986. The certification of candidate CRM is performed on the basis of worldwide interlaboratory comparison (ILC) and statistical evaluation of provided ILC data with some auxiliary procedures involved. This paper summarizes experiences and conclusions concerning adopted certification procedure coming form certification campaigns conducted by the INCT in order to produce CRMs of biological matrix in the years 1991, 2000 and 2004.

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Experimental

Preparation of candidate CRMs

In order to obtain dry biological material of appropriate homogeneity and stability, raw material collected was dried, ground, sieved, and fraction of particle size below 100 μm was isolated. The obtained powdered material was homogenized by mixing. After preliminary confirmation of homogeneity by means of XRF method, the material was distributed into containers. All containers with the candidate CRM were sterilized by electron beam irradiation with dose of approximately 30 kGy in order to ensure the long-term stability of the material. Then, final homogeneity was studied by determination of the concentration of selected elements applying instrumental neutron activation analysis (INAA). The results for six samples randomly taken from different containers were compared with six samples taken

from one container by means of the Fisher's test and *t*-Student's test. The minimum sample mass ensuring homogeneity of the material was established.

A procedure of water determination was established on the basis of water desorption curves obtained at selected temperatures in order to refer the analysis results to the same dry-weight state of the material.

Stability studies were performed within the period of 2 years. During this time, concentration of selected elements in two bottles was checked by INAA method. One bottle was stored in air-conditioned room at 20 °C and the second one in CO_2 incubator (ASAB) at 37 °C, 100% humidity and 5% CO_2. The observed trend in the data was examined by using regression analysis [7]. The details of applied procedures have been described elsewhere [8–11].

Interlaboratory comparisons

The intercomparison samples of the candidate reference materials and CRM unknown to participants were sent to the laboratories which had declared the intention to take part in the intercomparison. The participants were requested to do six independent determinations of so many elements as they could and report the results together with associated uncertainties expressed on a dry-weight basis after correction for blank. The details have been published previously [8–11].

Results and discussion

In the INCT, the intercomparison data provided by participating laboratories are statistically evaluated by means of the approach based on outlier's rejection procedure which utilizes concurrently statistical tests of Dixon, Grubbs, skewness and kurtosis at the significance level of 0.05, followed by the calculation of the overall arithmetic means after outlier rejection, standard deviations, standard errors and confidence intervals. The work of the applied procedure based on outlier's rejection was examined on ILC data when test materials of known true values of elemental composition or radionuclide contents were used [12]. In Table 1, certified values with their confidence limits for CTA-OTL-1 Oriental Tobacco Leaves obtained by applied procedure are compared with the Huber robust means and their confidence limits recommended by AMC [13, 14]. Very good agreement between both kinds of values is observed that confirms also validity of the adopted procedure of outlier's rejection. The certification ILC on elemental content of candidate CRM Oriental Tobacco Leaves was conducted in 1991 [8]. The CTA-OTL-1 was used in the course of ILCs conducted in the years 2000 and 2004 as a reference material accompanying new candidate RMs, and unknown to participants. The results obtained by laboratories for CTA-OTL-1 were compared with the certified values when available and used for creation of data set containing only results provided by the laboratories when confidence limits of the laboratory results overlapped with the confidence limits of the CRM. The second data set contained all results provided by participants. Both data sets were evaluated and calculated mean values were compared. As a certified value was recommended value obtained from the first data set when both values agreed and the overall mean and its confidence limit met the requirements of several qualification criteria [8–11]. In such a way, the use of CRM as a part of QA/QC confirms a correctness of applied procedure, as the good agreement of the certified values with those that could be assigned in the years 2000 and 2004 has been obtained [15]. On the other hand, the new CRM can be considering related to the CRM used in the ILC. Some examples of the results are shown in Fig. 1. Additionally, validity of the certified values is checked by the determination of selected element contents by high-accuracy ("definitive") RNAA methods developed in the INCT [16]. These methods are combination of neutron activation with the very selective and quantitative post-irradiation isolation of the desired radionuclide by column chromatography followed by gamma-ray spectrometric measurement. The elaborated RNAA methods fulfill the requirements of the CCQM definition of a primary ratio method of measurement (PMM) [17–19] and provide SI traceable values with very low levels of uncertainty. The comparison of the results obtained for CTA-OTL-1 in ILC in the years 1991, 2000 and 2004 with the results obtained by the high-accuracy potentially primary RNAA methods is shown in Fig. 2. As can be seen from Fig. 2, the certified values and the ILC values are in good agreement with the results obtained by the RNAA method proving additionally correctness of the certification procedure.

The use of worldwide ILC data for certification of candidate RMs results usually in relatively big data set of analytical results obtained by means of few analytical techniques. The agreement between mean values for different techniques applied is also very important assurance of validity of the certified value. Some of the elements listed in Table 1 like rare earths, Th, U, Se, Rb and V were determined only by NAA method in 1991. However, NAA has very well-recognized potential for accuracy [18–22]. It is based on a property of element nuclei, and the calibration is usually done with gravimetrically prepared elemental standards. When the INAA results are associated with uncertainties including all uncertainty sources, then INAA results should contribute to the traceability of the certified values to the SI units [20–22]. Because of much wider use of ICP-OES and ICP-MS methods, above-mentioned

Table 1 Comparison of certified values for CTA-OTL-1 with robust means

Element	Unit	Certified value and its confidence limit ($\alpha = 0.05$)	Robust mean and its confidence limit ($\alpha = 0.05$)	Number of laboratory means, n
Al	mg/kg	1740 ± 290	1862 ± 345	20
As	mg/kg	0.539 ± 0.060	0.575 ± 0.073	20
Ba	mg/kg	84.2 ± 11.5	89.6 ± 9.2	20
Br	mg/kg	9.28 ± 1.06	9.39 ± 0.58	15
Ca	mg/g	31.7 ± 1.2	31.5 ± 1.2	25
Cd	mg/kg	1.12 ± 0.12	1.20 ± 0.14	42
Ce	mg/kg	2.69 ± 0.30	2.65 ± 0.29	7
Co	mg/kg	0.879 ± 0.039	0.949 ± 0.061	42
Cr	mg/kg	2.59 ± 0.32	2.63 ± 0.30	43
Cs	mg/kg	0.18 ± 0.02	0.20 ± 0.04	17
Cu	mg/kg	14.1 ± 0.5	14.4 ± 0.6	53
Eu	mg/kg	0.038 ± 0.009	0.044 ± 0.012	9
K	mg/g	15.6 ± 0.5	15.6 ± 0.6	46
La	mg/kg	1.44 ± 0.16	1.50 ± 0.17	17
Li	mg/kg	23.0 ± 1.8	23.9 ± 1.3	13
Mg	mg/g	4.5 ± 0.2	4.6 ± 0.2	36
Mn	mg/kg	412 ± 14	417 ± 14	50
Ni	mg/kg	6.32 ± 0.65	6.33 ± 0.67	36
P	mg/kg	2892 ± 134	2874 ± 144	15
Pb	mg/kg	4.91 ± 0.80	4.97 ± 0.67	40
Rb	mg/kg	9.79 ± 1.27	10.24 ± 1.13	19
S	mg/kg	7316 ± 810	7080 ± 970	7
Se	mg/kg	0.153 ± 0.018	0.153 ± 0.021	9
Sm	mg/kg	0.229 ± 0.052	0.229 ± 0.062	6
Sr	mg/kg	210 ± 20	197 ± 23	26
Tb	mg/kg	0.032 ± 0.006	0.034 ± 0.013	6
Th	mg/kg	0.348 ± 0.054	0.347 ± 0.061	8
V	mg/kg	3.08 ± 0.42	3.28 ± 0.49	11
Zn	mg/kg	49.9 ± 2.4	50.06 ± 2.28	62

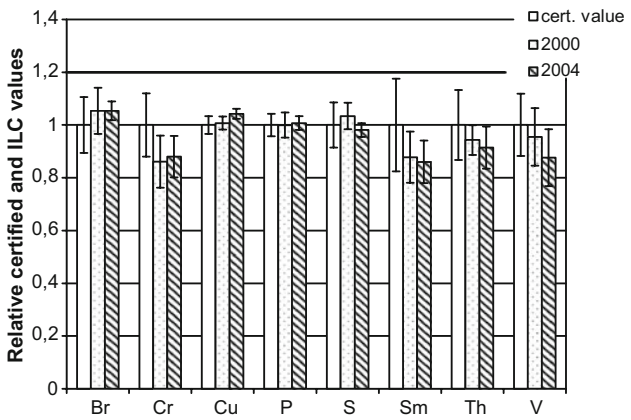

Fig. 1 Comparison of the reference and ILC values for selected elements. All values for individual element normalized to the certified value

elements have been determined by at least two methods in ILCs conducted lately. Changes in frequency of the use of different analytical techniques can be seen on the examples shown in Figs. 3, 4 and 5.

The performance of the laboratories can be generally recognized as slightly improving as can be seen on the example of U and Mo determination in the years 1991, 2000, 2004 (Fig. 6). The content of both above-mentioned elements has not been certified in CTA-OTL-1 because uncertainties of mean values calculated from ILC data did not fulfill qualification criteria. In 1991, Mo was determined the most frequently by NAA method. In the case of NAA method, the interfering nuclear reaction ^{235}U (n, f) ^{99}Mo has to be taken into account. It has been presumed that the observed spread of the ILC results for Mo was due to the lack or improper correction for the interfering reaction. In 2001 and 2004, all NAA results for Mo were corrected for fission reaction. The quantities of Mo

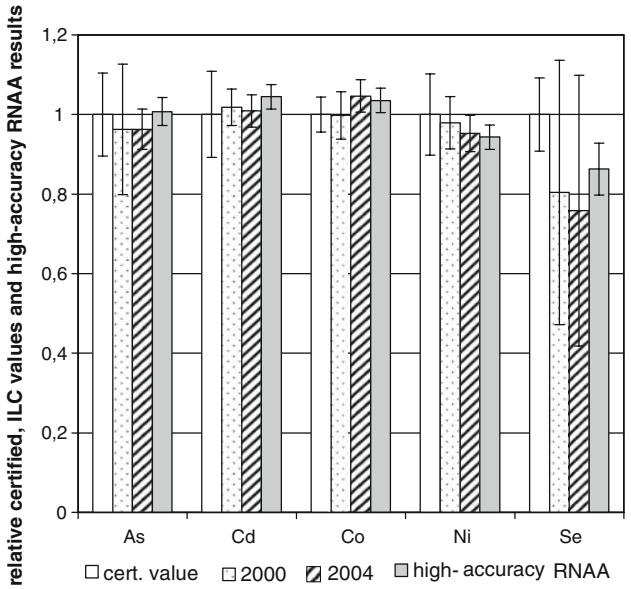

Fig. 2 Comparison of the reference and ILC values for selected elements with the results obtained by high-accuracy RNAA method; all values for individual element normalized to the certified value

determined by NAA and ICP-MS methods agreed well. Comparing the difference between potentially primary RNAA procedure values and the values and their uncertainties obtained for Mo and U in the years 2000 and 2004, one can see some progress in the overall performance of the participating laboratories.

Conclusions

In the INCT, the procedure of certification of candidate reference materials is based on the worldwide ILC. The provided data are statistically evaluated with the aid of procedure employing outlier's rejection. The adopted procedure of outlier's rejection works properly as can be seen comparing certified values with the robust means (Table 1). Certified and information values are assigned with the use of several qualification criteria. Additionally, the results of analysis by elaborated potentially primary RNAA method for selected elements and results of analysis of CRM accompanying candidate RMs are applied in the certification process as auxiliary actions for the quality assurance reasons. The agreement of the assigned values with the results obtained by the elaborated RNAA method confirms the validity of applied certification procedure. Good agreement of the certified values with the mean values obtained for the same CRM CTA-OTL-1 from ILCs in the period of over 15 years confirms the correctness and reliability of the adopted certification procedure as well as stability of CRM.

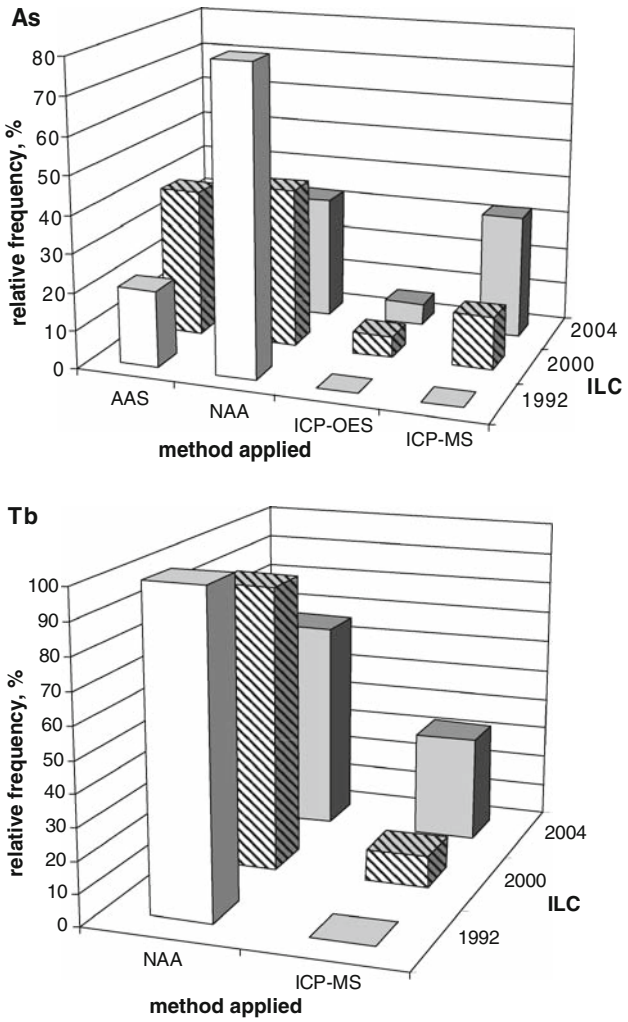

Fig. 3 Frequency of the use of analytical techniques for the determination of As and Tb in the years 1991, 2000 and 2004

In the current version of the VIM 3 [23] "the traceability (important property of CRM) cannot be provided by an inter-laboratory comparison, unless all individual measurement values used to establish the certified value are themselves traceable". So, there are two possibilities to establish traceability on the basis of ILC: one—using PMM for the certification, and second—using only traceable results for the certification. In the case of inorganic trace analysis, ID-MS is the only PMM acknowledged so far. That method cannot be used for monoisotopic elements. It makes the number of elements to be certified limited.

The INCT started its activity in the field of CRM in earlier 80-ties, when such demands were not obligatory. Even then, some efforts in order to confirm reliability of "recommended" or "certified" results obtained by the adopted method of ILC data evaluation were made by the application of additional elements of QA/QC. For that reason, (1) potentially primary RNAA procedures as well

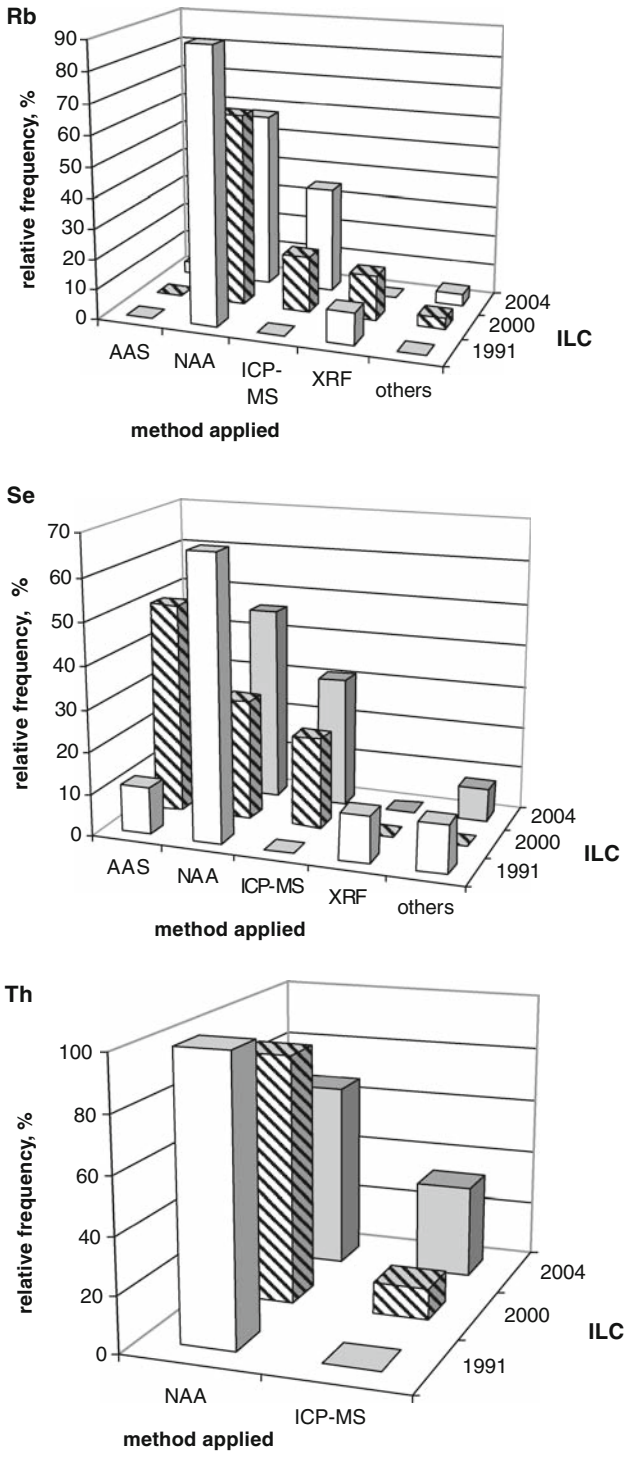

Fig. 4 Frequency of the use of analytical techniques for the determination of Rb, Se and Th in the years 1991, 2000 and 2004

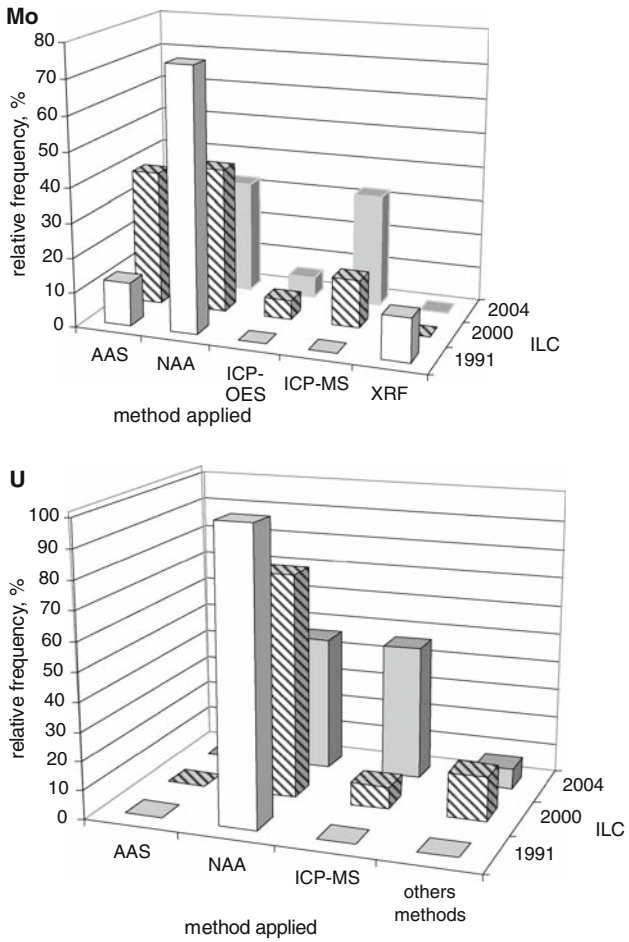

Fig. 5 Frequency of the use of analytical techniques for the determination of Mo and U in the years 1991, 2000 and 2004

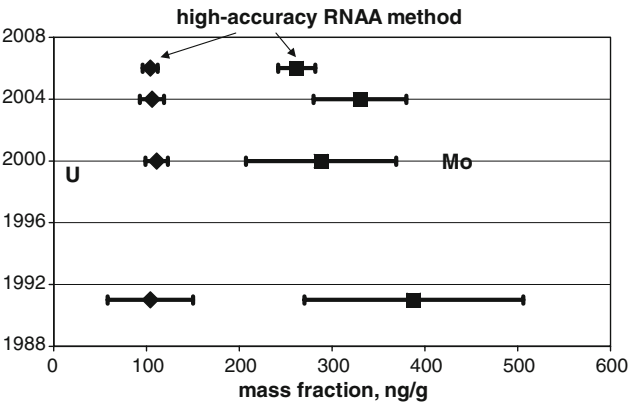

Fig. 6 Comparison of the mean values for U (*filled diamonds*) and Mo (*filled squares*) obtained from ILCs and obtained by high-accuracy RNAA method

as (2) existing CRM as an unknown sample were used. The above mentioned factors and demonstrated in the paper good agreement of the obtained results with those derived by another method of data evaluation (Table 1) proven that the certified values well represent true values of individual analytes in the CRMs.

Taking into account the demands of VIM 3 definitions [23], it would be necessary to adopt the applied certification procedures to the current requirements. Most of the CRMs present in the market do not fulfill the current

demands. However, our experience and experiences of our CRMs users testify that our CRMs have been successfully used for QA/QC purposes.

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