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Preparation of Three New Certified Reference Materials for Food and Environmental Analysis and Certification Using Laboratory Intercomparison as well as Primary Reference Measurement Procedures

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Abstract

Three new reference materials: MODAS-3 Herring Tissue (M-3 HerTis), MODAS-4 Cormorant Tissue (M-4 CormTis), and MODAS-5 Cod Tissue (M-5 CodTis) were prepared and certified on the basis of results of a worldwide intercomparison exercise. Independently of our proven method of establishing the certified and information values, the content of several essential and toxic elements was additionally determined by the use of ratio primary reference measurement procedures (definitive methods) based on radiochemical neutron activation analysis (RNAA) in the case of As, Cd, Co, Cr, Fe, Mo, Se, and U and isotope dilution mass spectrometry (IDMS) in the case of Hg, respectively. Good agreement of the established certified values and the results obtained by ratio primary reference measurement procedures confirmed the validity of the certification procedure. The total number of elements which could be certified amounted to 30, 21, 18 in M-3 HerTis, M-4 CormTis, and M-5 CodTis, respectively. The relative frequency of use of individual analytical techniques in this intercomparison campaign was calculated and discussed. Inductively coupled plasma mass spectrometry (ICP-MS) is now a dominant technique, followed by atomic absorption spectroscopy (AAS), NAA, and emission spectroscopy (ES). The decreasing share of NAA as compared to several earlier intercomparison exercises should be noticed. NAA is the only method in the array of highly sensitive methods of inorganic trace analysis, which is essentially free from blank. The lack of this method in the foreseeable future may be an obstacle in the prospective certification campaigns and may endanger the implementation of quality assurance in trace analysis.

Keywords Certified reference material · Interlaboratory comparison · Ratio primary reference measurement procedure · Definitive method · Inductively coupled plasma mass spectrometry · Neutron activation analysis

Introduction

Ecosphere is subject to constant evolution not only due to natural processes, local catastrophes as e.g. forest fire, tsunami, or eruption of volcanos but also due to the human influence like mining, transport, and industrial activity, waste disposal, etc. Human activity may cause substantial changes in the composition of water, air, soil, plants, and animal tissues what in consequence may lead to pollution of food products of vegetable and animal origin (Kabata-Pendias and Mukherjee 2007). Several elements e.g. Mn, Fe, Co, Cu, Zn, Mo, I, Ni, Se, and Sn have already been identified as essential to humans or toxic (Pb, Hg, As, Cd). The essentiality or toxicity of others e.g. rare

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earth elements (REE) was not unequivocally established although some researchers suggested that REE may play some biological role in the life systems (Ozaki et al. 1997; Tyler 2004). Chinese scientists maintained that REE accumulated in plants may enter via the food chain the bodies of animals and humans and affect regulating some biological functions (Qiu et al. 2005a, b). In this context, it is perhaps worth quoting the opinion of a medieval scientist and physician Paracelsus, reminded in the book describing the path of trace elements from soil to human (Kabata-Pendias and Mukherjee 2007), who wrote: "All substances are poisonous, there are none which is not a poison; the right dose is what differentiates a poison from a remedy". The growing concern about environmental pollution created the situation when it became necessary to monitor several components of the environment for the content of essential and toxic elements. We are living in an era when many important decisions (administrative, forensic, technological, ecological, biomedical, etc.) may depend upon the results of chemical analysis including also trace analysis (Dybczyński and Polkowska-Motrenko 2015; Dybczyński 2019). It is obvious that the correct decisions can be taken only when the analytical results on which they are based are reliable. The reliability of determination of several trace elements in various natural materials often leaves much to be desired. As an example, it can serve the data on the concentration levels of 18 trace elements in the blood plasma of apparently healthy individuals published in the literature over the time span of almost a quarter of century as compiled by Versieck and Cornelis (Versieck and Cornelis 1980). The dispersion of results for some essential elements like Ni, Mo, Mn, Co, and Cr reached a few orders of magnitude. It was expected that normally the concentrations of these elements should be kept within narrow limits because they are homeostatically controlled. Commenting on the observed disparities between the values reported by different investigators the authors of the compilation ascribe the probable reasons for inadequate sampling and sample handling or to defective analysis. Similar pessimistic conclusions can be drawn from the results of worldwide intercomparisons observed over a period of 40 years. The spread of results for "difficult" trace elements like As, Cd, Co, Hg, Pb, and many others exceeded, in the case of some of the intercomparison exercises, two, three or even five orders of magnitude (Dybczyński et.al 1979, Dybczyński 1980a, Dybczyński et.al. 1980b, Dybczyński 1981, Dybczyński et.al. 1989a, Dybczyński at.al. 1991, Dybczyński 1997, Dybczyński and Polkowska-Motrenko 2015, Dybczyński 2019). This indicates inadequate quality assurance in several laboratories. On the other hand, one should remember that trace analysis is a difficult task, often consisting of several steps, and there are many occasions to commit grave errors (Dybczyński 2002a).

Quality assurance (QA) of analytical procedures and quality control (QC) are essential for the quantitative measurements of elements in complex matrices. The correct practice to implement effectively those principles is the use of appropriate certified reference materials (CRMs) (Dybczyński and Polkowska-Motrenko 2015; Emons et al. 2006; Quevauviller and Griepink 1996). It is also necessary to use and incorporate CRMs in analytical protocols for the development and validation of new measurement methods and for the assessment of the reliability and comparability of the obtained results.

Good CRM should resemble as much as possible the real samples that are routinely analyzed. The feasible combinations of the type of matrix–concentration level(s) of the analyte(s) are practically unlimited. Therefore, the new CRMs should always be welcome. The availability of the CRMs certified for the content of trace and minor elements was summarized in several textbooks and review papers (Quevauviller and Griepink 1996, Dybczyński 2002b, Phillips et.al. 2007, Dybczyński and Polkowska-Motrenko 2015). Problems associated with the novel CRMs were recently discussed by Wise 2018. It should be noticed that currently on the market there is a very limited number of CRMs of fish origin for multi-elemental analysis. In fact, there are only 10 such materials in stock and available: 2 CRMs produced by the Joint Research Centre Geel (JRC Geel, Belgium), 2 CRMs produced by the International Atomic Energy Agency (IAEA, Monaco), 2 CRMs produced by the National Institute of Standards and Technology (NIST, USA), 2 CRMs produced by the National Research Council Canada (NRCC, Canada), and 2 CRMs produced by the National Metrology Institute in Japan (NMI, Japan) (*cf*. Table 1).

In the case of a cormorant matrix-matching sample, there is no certified material of such origin. It is well known that effective bioindicators of contamination in the environment

Table 1 Currently commercially available fish matrix-matching reference materials with the number of certified elements

Np	Code of CRM	Fish species	Number of certified elements
1	ERM-BB 422	Saithe	9
2	ERM-CE 101	Trout	6
3	IAEA-476	Mix of marine fish species	10
4	IAEA-436a	Tuna	10
5	NIST-1946	Trout	3
6	NIST-1947	Mix of lake fish species	8
7	NRCC DOLT-5	Dogfish	20
8	NRCC DORM-4	Dogfish	20
9	NMIJ CRM 7402a	Dogfish	9
10	NMIJ CRM 7403a	Swordfish	14

are fishes and piscivorous birds (e.g. cormorants, which occur at the top of aquatic food chain) as many elements (especially heavy metals) can be stored at higher concentrations in bodies of predators (Aazami and KianiMehr 2018; Houserova et al., 2007; Skoric et al., 2012). Matrix-matching fish and cormorant materials can be widely used for QA/QC of analysis result of metals pollution of food products of aquatic environment and thus to the risk assessment of human health. Moreover, reference materials available on the market (e.g. animal tissue) do not fully meet the needs of analytical laboratories, due to different compositions of the matrix, source, and geochemical characteristics, other natural and anthropogenic contaminants compared to real analyzed samples. In this paper, the preparation and certification of the three new CRMs: MODAS-3 Herring Tissue (M-3 HerTis), MODAS-4 Cormorant Tissue (M-4 CormTis), and MODAS-5 Cod Tissue (M-5 CodTis) intended for food, environmental, and biomedical trace analysis is reported. In the case of a few selected trace elements, the validity of the certified values, established in the course of elaboration of results of the worldwide interlaboratory comparison, was additionally confirmed by the results of "definitive methods" (Uriano and Gravatt 1977), which now, according to VIM 3, are called *"primary reference measurement procedures"* (ISO/IEC Guide 99:2007 2007).

The work was performed within the MODAS consortium, which was formed at the initiative of the late professor J. Namieśnik of the Gdańsk University of Technology. Other works executed within the frame of the consortium activity were already published (Baranowska et al. 2015, Baranowska et al. 2017, Rutkowska et al. 2018).

Methods and Materials

Strategy of Certification

Preparation and certification of reference materials is a complex task consisting of several stages which must be executed with utmost care to achieve the final success. The general approach used in our laboratory has been described in several earlier publications (Dybczyński et.al.1989a, Dybczyński et al. 1991, Dybczyński et al. 1993, Dybczyński 2002b, Polkowska-Motrenko et al.2010, Samczyński et al. 2012, Dybczyński and Polkowska-Motrenko 2015). All steps in the preparation and certification process are important but evaluation of the intercomparison results and assigning of certified ("recommended ") values has been considered to be the most critical one. In the early times of CRM production, practically every team of researchers employed his own method of elaboration of results. Some of these approaches were a combination of statistics and arbitrary decisions. Moreover, established "recommended" values were usually quoted without uncertainty limits. The review of these early times was published by S. Abbey (1977). Abbey himself was the supporter of some arbitrary decisions writing: "My philosophy is simple. The reliability of a result depends more on *who* produced it than on *how* it was done " (Abbey 1981). The program which we are using for the establishing of certified values on the basis of intercomparison results was originally devised for the Analytical Quality Control Service of the International Atomic Energy Agency (IAEA) (Dybczyński et al. 1978, Dybczyński 1980a). The aim was to create a fully objective method of data evaluation with the simultaneous setting free the general population from outlying results. This purpose was achieved by the concurrent use of four different statistical tests to minimize the so-called masking effects. The method was thoroughly tested and proved to yield very reliable results when applied to data sets from several intercomparison exercises, organized by IAEA on the determination of trace elements or low levels of radionuclides in which the "true values" were known (Dybczyński et al. 1978; Dybczyński, 1980a). Not every overall mean with its associated confidence limits (after rejection of outlying results) is automatically given the status of "certified value." To do so, several criteria must be simultaneously fulfilled. These criteria were formulated at the beginning of using this program (Dybczyński et al. 1979, Dybczyński 1980a, Dybczyński et al. 1980b), and with slight refinements (Dybczyński et al. 1989a, 1991; Samczyński et al. 2012; Dybczyński and Polkowska-Motrenko 2015) have been used also in this study. The advantages of our method were discussed in the literature (Abbey and Rousseau 1985). Several groups of researchers used this method for the certification of their reference materials (e.g., Hołyńska et al 1987, Kocman and Foley 1987).

The general strategy of preparation and certification of reference materials has been previously presented in detail in the literature. It was also used in the case of all CRMs issued by the Institute of Nuclear Chemistry and Technology (INCT) (Polkowska-Motrenko et al. 2010). These CRMs included materials with mineral matrix i.e. Apatite concentrate (CTA-AC-1) and Fine fly ash (CTA-FFA-1) (Dybczyński et al. 1989a, 1991) and a big group of materials with biological matrix, viz., Oriental tobacco leaves (CTA-OTL-1) (Dybczyński et al. 1993); Virginia tobacco leaves (CTA-VTL-2) (Dybczyński et al. 1998); Tea leaves (INCT-TL-1), and Mixed Polish herbs (INCT-MPH-2) (Dybczyński et al. 2004a, 2004b); Corn flour (INCT-CF-3) and Soya bean flour (INCT-SBF-4) (Polkowska-Motrenko et al. 2007); Oriental Basma tobacco leaves (INCT-OBTL-5), and Polish Virginia tobacco leaves (INCT-PVTL-6) (Samczyński et al. 2012).

Collection and Preparation of Materials

MODAS–3 Herring Tissue

Herring tissue, originating from fishes living in the North Sea, was prepared by the Gdańsk University of Technology. All operations were performed taking care to minimize any possibility of the contamination of future CRM. After freeze-drying and grinding the material was sieved through the 200-µm sieve. Homogenization was performed in the Institute of Nuclear Chemistry and Technology, (INCT). The whole lot of the material (ca. 70 kg) was placed in a 110 dm^3 polyethylene (PE) drum and mixed by rotating in three directions for 16 h. The homogenized material was distributed in 50 g portions to 100 cm^3 amber glass bottles with screw cap (future MODAS–3 Herring Tissue (M–3 HerTis) certified reference material) and in 10 g portions to 60 cm^3 (samples to be sent to the laboratories participating in the interlaboratory comparison), respectively. In order to ensure long-term stability of the new CRM, all containers with M–3 HerTis were sterilized by electron beam radiation (energy 13 MeV) from a linear accelerator LAEA-13. The dose amounted to approximately 27 kGy.

MODAS–4 Cormorant Tissue

Cormorant tissue, originating from the Czech Republic, was prepared by the Gdańsk University of Technology. After freeze-drying, grinding and sieving through the 200-µm sieve ca. 45 kg of the material was obtained. Homogenization, distribution, and sterilization were performed in the Institute of Nuclear Chemistry and Technology as described above.

MODAS–5 Cod Tissue

Cod tissue, originating from fishes living in the Baltic Sea, was prepared by the Gdańsk University of Technology. After freeze-drying, grinding and sieving through the 200-µm sieve ca. 70 kg of the material was obtained. Homogenization, distribution, and sterilization were performed in the Institute of Nuclear Chemistry and Technology as described above.

Testing of the Materials

Determination of Moisture Content

The moisture content ("dry state") was established individually for MODAS–3 Herring Tissue (M–3 HerTis), MODAS–4 Cormorant Tissue (M–4 CormTis), and MODAS–5 Cod Tissue (M–5 CodTis) materials on the basis of the water desorption curves recorded at several selected temperatures. For all the above materials, the adopted moisture determination procedure involved drying a 5 g subsample for 48 h at 85 °C.

Homogeneity Studies

Homogeneity testing of M–3 HerTis, M–4 CormTis, and M–5 CodTis was performed for the sample size of 100 mg. Two subsamples were taken from different eleven containers, chosen at random from the whole population of units of the given material. They were analyzed by inductively coupled plasma mass spectrometry (ICP-MS), whereas statistical evaluation of results was carried out applying the analysis of variance (ANOVA) approach (ISO Guide 35:2017 2017, Linsinger et al. 2000, 2001a; Van der Veen and Pauwels, 2000; Van der Veen et al. 2001a). The following analytical procedure was used. Microwave-assisted digestion of samples was applied by means of a multiwave 3000 high-pressure microwave system (Anton Paar GmbH). Known amounts (ca. 100 mg) of the materials were weighed into special Teflon vessels and at first 6 mL of conc. HNO_3 and 2 mL of 40% HF were added. When decomposition was completed, 6 mL portions of 4% H_3BO_3 solution were introduced to the samples and the vessels were re-sealed. This method ensures decomposition of silica and further removal of the excess of fluoride ions by complexation with boric acid. Solutions obtained as a result of microwave digestion were suitably diluted with 2% $HNO_3 + 5$ ng mL^{-1} In-115 (internal standard) and then the mass fraction of selected elements was determined by ICP-MS. On the basis of obtained analytical results, the so-called mean squares among containers (MS_a) as well as within containers (MS_w) were calculated.

The standard uncertainty resulting from the inhomogeneity of M–3 HerTis, M–4 CormTis, and M–5 CodTis were evaluated using the ANOVA method (ISO Guide 35:2017 2017, Van der Veen et al. 2001a, b). Its estimation (so-called between bottle variance) was calculated from the MS_a and MS_w values (ISO Guide 35:2017 2017, Van der Veen et al. 2001a, b).

Stability Studies

Long-term stability studies of newly issued CRMs are mandatory for their manufacturers (Ellison et al. 2001, ISO 17,034 2016, ISO Guide 35:2017 2017, Linsinger et al. 2000, Linsinger et al. 2001a, Linsinger et al. 2001b, Pauwels et al. 1998, Van der Veen et al. 2001b). In the case of M–3 HerTis, M–4 CormTis, and M–5 CodTis, it was realized by comparing the results obtained for samples stored under controlled conditions i.e. in the air-conditioned room at 20 °C (normal storage). Samples of the given material were taken from the randomly chosen container after 0, 2, 4, 6, 10, 12,

and 15 months of storage. Mass fractions of selected elements were determined by ICP-MS in order to establish the relationship between the content of a given element (C) and time (x). Assuming a linear regression model of degradation, an estimate was fitted using the least square method (Linsinger et. al. 2001a, Linsinger et al. 2001b, Pauwels et al. 1998, Van der Veen et al. 2001b):

$$C = a + bx \quad (1)$$

where b is the slope of the line (degradation rate). Long-term stability of the material was assessed by comparing $|b|/u_b$ to the value of the t-test ($\alpha = 0.05$ and $n - 2$ degrees of freedom) where u_b is the standard deviation of the slope of the fitted regression line (Linsinger et al. 2001a, b; Van der Veen et al. 2001b, ISO Guide 35:2017 2017).

The standard uncertainties associated with the long-term stability of M–3 HerTis, M–4 CormTis, and M–5 CodTis were determined on the basis of the obtained regression lines, calculating the standard deviation of their slope (ISO Guide 35:2017 2017, Linsinger et al. 2001a, Linsinger et al. 2001b).

The stability of reference materials in transport conditions (short-term stability) was also investigated. The materials were stored in CO_2 incubator at 37 °C, 100% humidity, and 5% CO_2 for 2 mounts and the changes in the concentration of selected elements were examined.

Element Content Characterization of the Materials

Interlaboratory Comparison

In order to certify the trace elements content in M–3 HerTis, M–4 CormTis, and M–5 CodTis candidate reference materials, a worldwide interlaboratory comparison was organized. The number of participating laboratories from eleven countries was 47, 46, and 50, respectively, providing the data for over 60 elements.

Samples of the mass 10 g of the candidate reference materials (so-called intercomparison samples) together with the information sheets were sent to the laboratories, which had previously confirmed participation in this study. It was requested to make at least three, but preferably six separate determinations for as many elements as they were able to, using a method of choice. The results should have been provided electronically in the specially designed MS Excel file (sent by e-mail). The participants were requested to report the determined concentrations (mass fractions) of elements as net values i.e. after correcting for blank (if any), moisture content, etc. The laboratories were also asked to provide for each element the following information: the average mass of the analyzed sample, detection limit of the method used, and the combined standard uncertainty together with the short description of the whole analytical procedure. This information was expected to contain the sample pretreatment method, preconcentration and separation procedure (if any), the technique of quantitative determination, and certified reference material(s) used for the quality control. In order to secure anonymity, the laboratories were coded and the code number has been known exclusively to the participant himself and to the organizers.

The components of the whole analytical procedure were also coded as shown in Table 2 for presumptive further more detailed analysis of the data. The excerpt of the so constructed database is shown in Fig. 1. In order to avoid any possible errors, the results of each laboratory were extracted individually from the database and sent back to the participant for checking. In the case of indicating any discrepancies, all necessary corrections were immediately made.

Data Evaluation

Results delivered by the laboratories participating in the interlaboratory comparison were organized in the form of a large database. It had a special structure, enabling work with the AQCS-1 package—the software employed for the data processing (Szopa et al. 1996). Analogously like in the case of our former certification campaigns, the database was subjected to statistical evaluation. The essential part of this process is the outlier's rejection procedure. The population of laboratory averages for a given element is examined applying four statistical tests, namely those of Dixon (D), Grubbs (G), Skewness (S), and Kurtosis (K) at the significance level of 0.05. When a given result is classified as an outlier by any test, it is rejected from the population until no outlying result is detected. The final value of the overall mean is calculated from laboratory averages remaining after outliers' rejection (*c.f.* Figure 2).

Results and Discussion

Materials Homogeneity and Stability Study

The candidate reference materials were prepared in such a way that they met the requirements of ISO Guide 35 (ISO 35:2017 2017) and ISO 17,034 (ISO 17034:2016 2016). Their homogeneity and stability were tested.

To assess the homogeneity, the minimum sample mass for which a given material can be considered homogeneous were specified, as well as the uncertainty associated with heterogeneity.

Natural matrix CRMs are always inhomogeneous on a microscopical scale. Apparent homogeneity is achieved by grinding, sieving, and mixing the material. When a great number of individual particles are present in the subsample of a given mass, then it can be assumed that all such subsamples have the same average elemental composition. Using a very simplified model (Harris and Kratochvil 1973,

Table 2 Method codes for pretreatment, preconcentration and/or separation and the technique for the quantitative determination

Pretreatment
0 – Not communicated
1 – No pretreatment
2 – Pelletizing, briquetting
3 – Acid dissolution (normal pressure or not specified)
4 – Acid dissolution (pressure bomb)
5 – Acid dissolution (microwave technique)
6 – Fusion
7 – Grinding
8 – Combustion, ignition, pyrolysis
9 – Pyrohydrolysis
Preconcentration and/or separation
0 – Not communicated
1 – No preconcentration or separation used
2 – Chemical separation (general statement without details)
3 – Precipitation, coprecipitation
4 – Extraction, extraction chromatography
5 – Ion exchange, adsorption
6 – Distillation, volatilization
7 – Electrolysis, electrodeposition
8 – Other methods
Quantitative determination
A0 – Atomic absorption (AAS general)
A1 – AAS (flame technique)
A2 – AAS (electrothermal atomization)
A3 – AAS (cold vapor technique)
A4 – AAS (hydride generation)
B0 – Not communicated
E0 – Atomic emission spectroscopy (AES general)
E1 – AES (flame)
E2 – AES (ICP)
E3 – DCP (direct current plasma)
E4 – DC arc
E5 – HT spark
E6 – AES-ICP (hydride generation
M0 – Mass spectrometry (MS general)
M1 – SSMS
M2 – ICP-MS
N0 – Neutron activation analysis (NAA general)
N1 – INAA (thermal neutrons)*
N2 – INAA (epithermal neutrons)*
N3 – RNAA (thermal neutrons)*
N4 – RNAA (epithermal neutrons)*
N5 – INAA (delayed neutron counting)
O1 – Other methods
O2 – Gravimetric analysis
O3 – Volumetric analysis
O4 – Turbidimetry
R0 – Radiometric analysis
R1 – Radiometric analysis—gamma ray spectrometry
R2 – Radiometric analysis—alpha ray spectrometry
S0 – Molecular spectrometry
S1 – Spectrophotometry
S2 – Colorimetry
S3 – Luminescence, fluorimetry, spectrofluorimetry
S4 – IR spectrometry
V0 – Voltammetry and other electrochemical methods (general)
V1 – Voltammetry
V2 – Ion-selective electrodes
X0 – X-ray fluorescence (XRF general)
X1 – XRF energy dispersive
X2 – XRF wavelength dispersive
X3 – PIXE
X4 – PIGE

* with γ-ray and/or X-ray spectrometry

Dybczyński et.al. 2000, Dybczyński et.al. 2001), it was possible to derive a formula for the relative standard deviation due to inhomogeneity (sampling error), R_s:

$$R_s = \sqrt{\frac{K_s}{m_{sample}}} = 10^2 \sqrt{\frac{m_{particle}}{C_A . m_{sample}}} \quad (2)$$

where K_s is Ingamells sampling constant (Ingamells and Switzer 1973), m_{sample} is the sample mass (g), $m_{particle}$ is the average mass of a single particle (g), and C_A is the concentration (mass fraction) of an element A (g g^{-1}). So, the sampling error is directly proportional to the square root of the mass of the single particle and inversely proportional to the square root of the mass fraction of an analyte (at constant sample mass). The sampling error increases strongly with the increase of dimension of the single particle ($m_{particle}$ is roughly proportional to the third power of particle's dimension) (Dybczyński et al. 2000, 2001; Dybczyński 2015).

As far as our previous CRMs are concerned, the minimum sample mass for which homogeneity was proved, usually amounted to 100 mg (Dybczyński et al. 1991, 1993; Dybczyński et al. 2004a, b; Polkowska-Motrenko et al. 2007; Samczyński et al. 2012). However, in one case (Virginia tobacco leaves CTA-VTL-2), i.e., for the material with a specially fine particle size (15–35 μm), thorough investigations revealed that the material was sufficiently homogenous even for the sample sizes of single milligrams (Dybczyński et al. 1998). Because of the specific properties of the materials being subject of this work, it was difficult to obtain a significant amount of particles much smaller than 200 μm. Basing on our previous experience, it was decided that the rational sample mass for which the homogeneity could be guaranteed should be around 100 mg. On the basis of obtained results (*c.f.* Table 3), it was stated that the materials are homogenous for the sample size of 100 mg or greater.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	Lab. code	Sample code	Ele-ment	unit	Result 1	Result 2	Result 3	Result 4	Result 5	Result 6	Sample size (mg)	Detection limit	Method code	Uncert. (%)	CRM	
2																
3																
4		M-5 CodTis	Cu	ppm												
5	1		Cu	ppm	1.33	1.33	1.40	1.37	1.37	1.37	200	0.01	5- 1-A2		No	
6	3		Cu	ppm	1.19	1.36	1.16	1.39	1.20	1.41	500-1000	1	5- 1-A1	15	Yes	
7	4		Cu	ppm	1.57	1.62	1.72				400	1.25	5- 1-A1	4.9	Yes	
8	5		Cu	ppm	1.42	1.44	1.44	1.45	1.48	1.51	500 -1000		5- 1-E2	20	Yes	
9	5A		Cu	ppm	1.61	1.70	1.52	1.40	1.48	1.47	500 -1000		5- 1-M2	20	Yes	
10	7		Cu	ppm	2.07	1.20	1.21				200	0.27	4- 1-M2	20.0	Yes	
11	7A		Cu	ppm	0.55	0.48	0.50				200	0.12	4- 1-E2	15.0	Yes	
12	7B		Cu	ppm	2.2	4.4	1.9	2.5			500	2	2- 1-X0	20.0	Yes	
13	8		Cu	ppm	1.42	1.52	1.35	1.33	1.49	1.33			5- 1-A2	18	No	
14	9		Cu	ppm	1.2	1.2	1.2				150	0.102	5- 1-M2	3	No	
15	9A		Cu	ppm	1.2	1.1	1.1				150	0.102	5- 1-M2	3	No	
16	10		Cu	ppm	1.35	1.37	1.29	1.44	1.45	1.38	850	0.0004	5- 1-E2	5	Yes	
17	12		Cu	ppm	1.3	1.2	1.2	1.2	1.3	1.3	513	0.1	5- 1-E2	12	Yes	
18	13		Cu	ppm	1.35	1.40	1.35				300	0.16	5- 1-A2	8.03	Yes	
19	14		Cu	ppm	1.32	1.30	1.36				500	0.03	5- 1-M2		Yes	
20	17		Cu	ppm	1.50	1.92	1.33	1.60			50	0.21	4- 1-M2	16	Yes	
21	17B		Cu	ppm	3.0	3.8	2.7	2.4	2.6	2.4	500	2	2- 1-X0	18	Yes	
22	18		Cu	ppm	1.56	1.46	1.55	1.53	1.64	1.48	0.700	0.014	5- 1-M2	15	Yes	
23	19		Cu	ppm	1.5	1.6	2.2	2.4	1.4	2.0	1000	0.040	5- 1-E2	15	Yes	
24	20		Cu	ppm	1.38	1.34	1.36	1.36	1.37	1.35	250	0.0090	5- 1-M2	0.85	Yes	
25	22		Cu	ppm	28	35	32	36	39	37	200	0.015	5- 1-A1	12	Yes	
26	23		Cu	ppm	1.71	1.68	1.68	1.66	1.81	1.77	250	0.05	5- 1-M2	25	Yes	
27	24		Cu	ppm	1.21	1.25	1.27	1.18	1.30	1.28	450	0.021	5- 1-V1	10	Yes	
28	25		Cu	ppm	1.43	1.34	1.58	1.34			500	0.32	5- 1-E2	11	Yes	
29	26		Cu	ppm	1.47	1.30	1.33				1000	0.43	5- 1-A1	10	Yes	
30	28		Cu	ppm	1.41	1.32	1.27	1.45	1.39	1.43		0.002	5- 1-A0	12.3	No	

Database 1 | Database 1A | M-5 CodTis | M-5 CodTis (search) | M-5 CodTis - NAA | M-5 CodTis - AAS | M-5 CodTis - ES | M-5 CodTis - ICP-MS | M-5 CodTis - XRF | M-5 Cod

Fig. 1 A fragment of the computer database created from results supplied by participating laboratories

The evaluated standard uncertainty due to inhomogeneity amounted to 2.00%, 1.90%, and 1.80% for the M-3 HerTis, M-4 CormTis, and M-5 CodTis, respectively.

Long-term stability studies of newly issued CRMs were performed in accordance with the recommendation for the manufacturers (Ellison et al. 2001, ISO 17,034 2016, ISO Guide 35:2017 2017, Linsinger et al. 2000, Linsinger et al. 2001a, b, Pauwels et al. 1998, Van der Veen et al. 2001b). On the basis of a long-term stability study, it was found that the presented CRMs should be stored at room temperature,

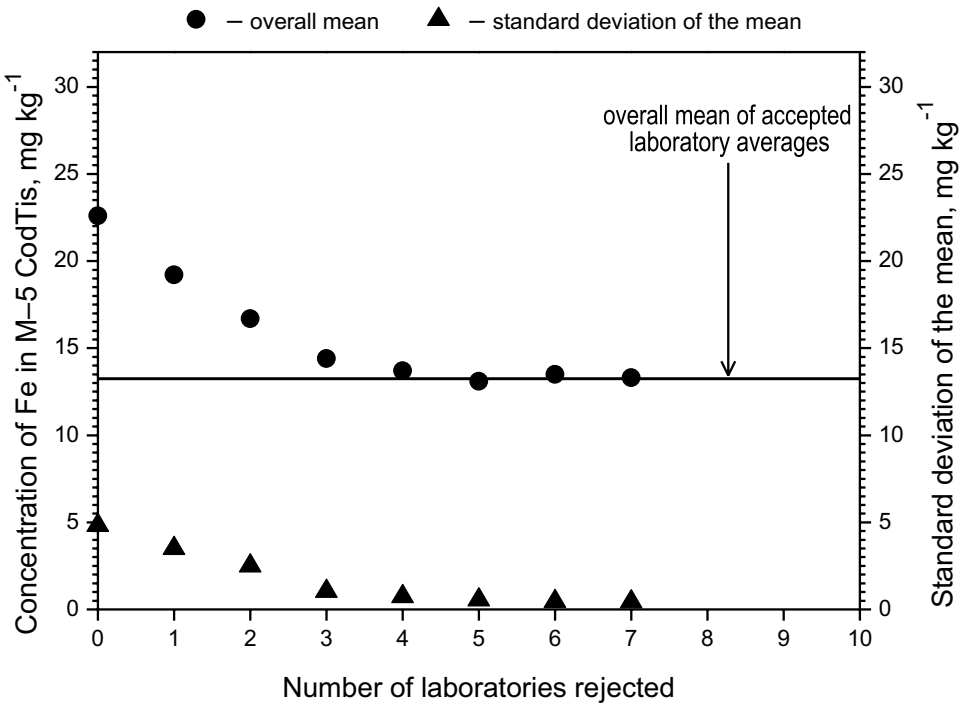

Fig. 2 Changes in the overall mean and standard deviation of the mean for Fe in M–5 CodTis observed while executing the outlier's rejection procedure

Table 3 Homogeneity testing of the candidate reference materials M–3 HerTis, M–4 CormTis, and M–5 HerTis for 100 mg sample by ICP-MS using analysis of variance (ANOVA)

Element	MS_a	a	MS_w	n_i	$F^{*)}$	$F_{0.05}$
M–3 HerTis						
Cd	0.00205	11	0.00218	2	1.064 < 2.854	
Mg	12,797.07	11	13,478.71	2	1.053 < 2.854	
Mn	0.0574	11	0.1000	2	1.742 < 2.854	
Sr	8.1597	11	7.7899	2	1.309 < 2.854	
V	0.00275	11	0.00320	2	1.162 < 2.854	
Zn	17.767	11	21.148	2	1.190 < 2.854	
M–4 CormTis						
Cd	0.000031	11	0.000037	2	1.180 < 2.854	
Co	0.000169	11	0.000163	2	1.037 < 2.854	
Cu	8.1597	11	7.7899	2	1.047 < 2.854	
Mn	0.00763	11	0.00985	2	1.292 < 2.854	
V	0.000005	11	0.000008	2	1.469 < 2.854	
Zn	2.6860	11	3.3951	2	1.264 < 2.854	
M–5 HerTis						
Cu	0.43008	11	0.62719	2	1.458 < 2.854	
Fe	13.804	10	16.212	2	1.174 < 2.854	
Mn	0.01319	11	0.01708	2	1.295 < 2.854	
Sr	0.19697	11	0.25752	2	1.307 < 2.854	
V	0.000033	11	0.000052	2	1.565 < 2.854	
Zn	0.8834	11	1.5657	2	1.772 < 2.854	

MS_a mean squares among containers, MS_w mean squares within containers, a the number of containers, n_i the number of subsamples taken from the container, $F = \frac{MS_{a(w)}}{MS_{w(a)}} > 1$,

$F_{0.05}$ critical value of the Fisher's test at significance level α=0.05 and degrees of freedom: $f_1 = a - 1; f_2 = \sum_{i=1}^{a} n_i - a$,

protected from light, in a tightly closed container. In such conditions, it remains stable at least 5 years since the year of production. The values of standard uncertainty resulting from long-term storage of the materials were estimated to be 1.10%, 1.13%, and 1.07%, respectively. The uncertainty related to the short-term stability of the materials was found to be not significant and can be ignored. Also the dry states of the new CRMs were defined on the basis of a plateau of the water desorption curves. The reliable and reproducible procedure for the determination of moisture content was developed for all the materials to enable the analytical results to be related to the same state of the examined material.

Assigning of the Certified and Information Values

As the candidate reference materials met the criteria, it was possible to conduct an interlaboratory comparison and use the obtained data to assign the certified values for concentration (mass fraction) of elements. Those values were assigned when the overall mean calculated from laboratory averages remaining after outliers' rejection met the quality criteria for the analytical uncertainty, the number of results, and number of analytical methods (Polkowska-Motrenko et al. 2010).

Each certified value has been assigned its combined uncertainty. In accordance with current ISO standards (ISO Guide 35:2017 2017, Linsinger et al. 2000), the combined standard uncertainty of the certified value u_c, is calculated taking into account the following four components:

$$u_c = \sqrt{u_{\text{interlab}}^2 + u_{\text{lstab}}^2 + u_{\text{inhom}}^2 + u_{\text{m}}^2} \quad (3)$$

where u_{interlab} is standard analytical uncertainty estimated as the standard deviation of the overall mean, u_{lstab} the standard uncertainty estimated from the long-term stability studies, u_{inhom} the standard uncertainty estimated from the homogeneity studies, and u_{m} the standard uncertainty due to moisture determination. Afterwards, the expanded uncertainty (U), which corresponds to 95% confidence level, is calculated as the product of u_c and the coverage factor $k=t_{0.05}$ (Student's t-test parameter for α=0.05 and n-1 degrees of freedom, where n is the number of laboratory averages). Certified values must always be quoted together with their uncertainties: $X \pm U$. Traceability to the International System of Units (SI) was maintained, because participating laboratories along with the analysis of the candidate reference materials analyzed also CRMs of a similar matrix. Additionally, the traceability was established by use, when available, ratio primary reference measurement procedures (definitive methods) based on radiochemical neutron activation analysis (RNAA) and isotope dilution mass spectrometry (IDMS) as well as neutron activation analysis (NAA) procedures calibrated against pure metals or oxides with full uncertainty budget. Certified values with their uncertainties are quoted in Tables 4 and 5.

Several elements in M–3 HerTis, M–4 CormTis, and M–5 CodTis did not meet the criteria for the certified values however fulfilled the criterion for assigning the information values. The information values (*cf.* Table 5) are quoted as numbers only. Information value provides some idea about the mass fraction of a given element in the material, but should never be made equal with the certified value.

Finally, it was possible to assign the certified concentration (mass fraction) value to 30 elements in MODAS–3 Herring Tissue, 21 in MODAS–4 Cormorant Tissue, and 18 in MODAS–5 Cod Tissue, respectively. The information values were assigned for 3, 4, and 8 elements in the case of M-3 HerTis, M-4 CormTis, and M-5 CodTis, respectively.

Primary Reference Measurement Procedures (Definitive Methods) as an Auxiliary Tool in the Process of Certification of the Candidate Reference Materials.

Definitive methods (Uriano and Gravatt 1977) or primary reference measurement procedures (ISO/IEC Guide 99:2007 2007) are the methods of the highest metrological quality,

Table 4 Certified values (X ± U) for MODAS–3, MODAS–4, and MODAS–5

Major and minor elements		Trace elements (1–1000 mg kg^{-1})		Trace elements (below 1 mg kg^{-1})	
Element	Mass fraction (wt. %)	Element	Mass fraction (mg kg^{-1})	Element	Mass fraction (μg kg^{-1})
MODAS–3 Herring tissue (M–3 HerTis)					
Cl	2.68 ± 0.46	As	9.22 ± 0.79	Ag	36 ± 5
K	1.17 ± 0.12	Ba	2.71 ± 0.28	Cd	325 ± 30
Mg	0.30 ± 0.02	Br	111 ± 11	Co	69 ± 6
Na	1.92 ± 0.17	Cu	3.19 ± 0.22	Cr	919 ± 105
P	2.35 ± 0.39	Fe	190 ± 13	Cs	83.3 ± 7.5
S	0.93 ± 0.10	Mn	5.78 ± 0.61	Hg	227 ± 21
		Rb	2.32 ± 0.19	Li	896 ± 113
		Se	2.62 ± 0.24	Mo	127 ± 20
		Sr	192 ± 15	Ni	316 ± 49
		Zn	111 ± 6	Pb	104 ± 13
				Sb	15.8 ± 3.8
				Sc*	3.2 ± 0.4
				U	75.2 ± 8.2
				V*	782 ± 112
MODAS–4 Cormorant tissue (M–4 CormTis)					
K	1.19 ± 0.08	Br	11.1 ± 0.9	As	121 ± 12
Mg	0.10 ± 0.01	Cu	19.5 ± 1.2	Cd	17.2 ± 2.1
Na	0.22 ± 0.02	Fe	281 ± 16	Co	40.4 ± 3.9
P	0.89 ± 0.14	Hg	2.20 ± 0.14	Cs	35.4 ± 4.6
S	1.04 ± 0.11	Mn	2.12 ± 0.18	Sb	67 ± 12
		Pb	2.33 ± 0.28	V*	7.8 ± 1.2
		Rb	13.3 ± 0.8		
		Se	1.27 ± 0.12		
		Sr	0.24 ± 0.03		
		Zn	63.4 ± 3.5		
MODAS–5 Cod tissue (M–5 CodTis)					
Cl	0.41 ± 0.04	As	1.65 ± 0.26	Ba	162 ± 28
K	1.92 ± 0.12	Br	24.8 ± 3.3	Cs	59 ± 5
Mg	0.12 ± 0.02	Cu	1.38 ± 0.09	Hg	310 ± 22
Na	0.34 ± 0.02	Fe	13.3 ± 1.1	Mn	921 ± 75
P	0.96 ± 0.12	Rb	4.54 ± 0.31		
S	1.05 ± 0.16	Se	1.33 ± 0.10		
		Sr	4.07 ± 0.36		
		Zn	20.2 ± 1.1		

*Certified on the basis of results by single analytical method

which are used to check the accuracy of other routine methods employed in the chemical analysis of elements. Isotope dilution mass spectrometry (IDMS) is a well-established technique used for the very accurate determination of trace

Table 5 Information values (X ± U) for MODAS–3, MODAS–4, and MODAS–5

MODAS–3 Herring tissue (M–3 HerTis)			MODAS–4 Cormorant tissue (M–4 CormTis)			MODAS–5 Cod tissue (M–5 CodTis)		
Element	Mass fraction	Unit	Element	Mass fraction	Unit	Element	Mass fraction	Unit
Ca	3.69	wt. %	Ag	3.8	μg kg^{-1}	Bi	7.0	μg kg^{-1}
Sm	1.8	μg kg^{-1}	Ca	258	mg kg^{-1}	Ca	0.11	wt.%
Y	9.6	μg kg^{-1}	Cr	158	μg kg^{-1}	Cd	5.0	μg kg^{-1}
			Mo	91	μg kg^{-1}	Co	14	μg kg^{-1}
						Cr	201	μg kg^{-1}
						Li	26	μg kg^{-1}
						Ni	136	μg kg^{-1}
						Pb	45	μg kg^{-1}

elements (De Bievre 1993; Vogl 2007). The other methods of similar metrological quality which can be used in the field of trace analysis are ratio primary reference measurement procedures (RPRMP) or definitive methods based on radiochemical neutron activation analysis (RNAA) (Dybczyński et al. 1989b, 2007, 2014; Dybczyński 1997, 2015). The essence of these methods is the combination of neutron activation with the post-irradiation selective and quantitative isolation of the desired radionuclide by column chromatography followed by γ-ray spectrometric measurement.

These methods have the advantage over the IDMS that they can be devised and used also in the case of monoisotopic elements. Both varieties of RPRMP (definitive methods) were used in this study for the determination of selected trace elements, employing the procedures previously devised for arsenic (Chajduk and Dybczyński 2010), cadmium (Samczyński and Dybczyński 1996), cobalt (Polkowska-Motrenko et al. 2004; Dybczyński and Danko 1994), chromium (Zuba and Polkowska-Motrenko 2019), iron (Dybczyński et al. 2012), mercury (Bulska et al. 2017), molybdenum (Danko and Dybczyński 1997), selenium (Chajduk et al. 2008), and uranium (Danko and Dybczyński 1997). Results by the definitive methods were not included in the population of intercomparison results but served for independent validation of the process of certification (*cf.* Table 6). As can be inferred from Table 6 in all cases, in which we managed to perform the measurements, there is a good agreement between the certified value and the result obtained by RPRMP (the confidence interval of the result by definitive method at 95% confidence level overlaps the uncertainty range of the certified value). The graphical presentation of selected examples together with the original range of results sent in by participants of the intercomparison is shown in Fig. 3.

The Share of Analytical Techniques in the Certification Process Now, in the Past, Its Evolution, and Consequences

Each certification campaign provides valuable information concerning analytical techniques employed when determining the individual elemental content in the candidate reference materials. Using the descriptions of the analytical procedure as supplied by the participating laboratories it was possible to calculate the relative frequency of the use of particular analytical techniques employed in this study. Graphical presentation of the share of the methods applied when analyzing M–4 CormTis is shown in Fig. 4. In the case of M–3 HerTis and M–5 Cod-Tis, the picture is roughly the same. As is evident, four methods occupy a predominant position in the certification, namely, inductive coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), neutron activation

Table 6 Comparison of the certified and/or information value with the result obtained with the aid of the ratio primary reference measurement procedure (RPRMP) for some elements in the materials M–3 HerTis, M–4 CormTis, and M–5 CodTis. The uncertainties are expanded uncertainties at 95% confidence level

Material	Cd		Co		Fe		Cr		Mo		U		As		Se		Hg	
	Cert./ inform value	RNAA RPRMP	Cert./ inform value	RNAA RPRMP	Cert./ inform value	RNAA RPRMP	Cert./ inform value	RNAA RPRMP	Cert./ inform value	RNAA RPRMP	Cert./ inform value	RNAA RPRMP	Cert./ inform value	RNAA RPRMP	Cert./ inform value	RNAA RPRMP	Cert./ inform value	IDMS
M–3 HerTis	325 ± 30 ng g^{-1}	330 ± 17 ng g^{-1}	69 ± 6 ng g^{-1}	66 ± 2 ng g^{-1}	190 ± 13 mg kg^{-1}	187 ± 10 mg kg^{-1}	919 ± 105 ng g^{-1}	1030 ± 30 ng g^{-1}	127 ± 20 ng g^{-1}	134 ± 13 ng g^{-1}	75.2 ± 8.2 ng g^{-1}	77.0 ± 3 ng g^{-1}	9.22 ± 0.79 mg kg^{-1}	9.81 ± 0.25 mg kg^{-1}	2.62 ± 0.24 mg kg^{-1}	2.45 ± 0.10 mg kg^{-1}	227 ± 21 ng g^{-1}	236 ± 14 ng g^{-1}
M–4 CormTis	17.2 ± 2.1 ng g^{-1}	17.5 ± 1.2 ng g^{-1}	40.4 ± 3.9 ng g^{-1}	45.2 ± 1.1 ng g^{-1}	281 ± 16 mg kg^{-1}	269 ± 26 mg kg^{-1}	160 ng g^{-1}	147 ± 4 91 ng g^{-1}		103 ± 39 ng g^{-1}	–	–	121 ± 12 ng g^{-1}	–	1.27 ± 0.12 mg kg^{-1}	1.21 ± 0.05 mg kg^{-1}	2.20 ± 0.14 mg kg^{-1}	2.23 ± 0.05 mg kg^{-1}
M–5 CodTis	5 ng g^{-1}	–	19 ng g^{-1}	–	13.3 ± 1.1 mg kg^{-1}	13.8 ± 1.7 mg kg^{-1}	205 ng g^{-1}	205 ± 5 – ng g^{-1}			–	–	1.65 ± 0.26 mg kg^{-1}	1.83 ± 0.05 mg kg^{-1}	1.33 ± 0.10 mg kg^{-1}	1.26 ± 0.05 mg kg^{-1}	310 ± 22 ng g^{-1}	303 ± 15 ng g^{-1}

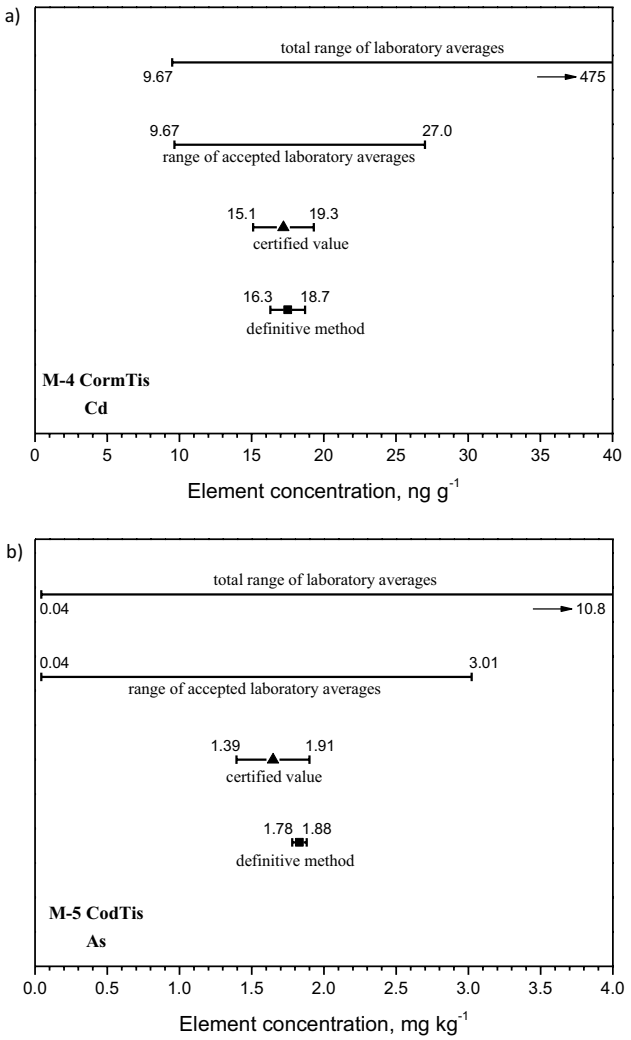

Fig. 3 **a** Comparison of the certified value and its confidence limits for Cd in M–4 CormTis with the results obtained using the definitive method (ratio primary reference measurement procedure) on the background of the original range of results submitted by participating laboratories. The "range of accepted laboratory averages" refers to the data after rejection of outlying results. **b** Comparison of the certified value and its confidence limits for As in M–5 CodTis with the results obtained using the definitive method (ratio primary reference measurement procedure) on the background of the original range of results submitted by participating laboratories. The "range of accepted laboratory averages" refers to the data after rejection of outlying results

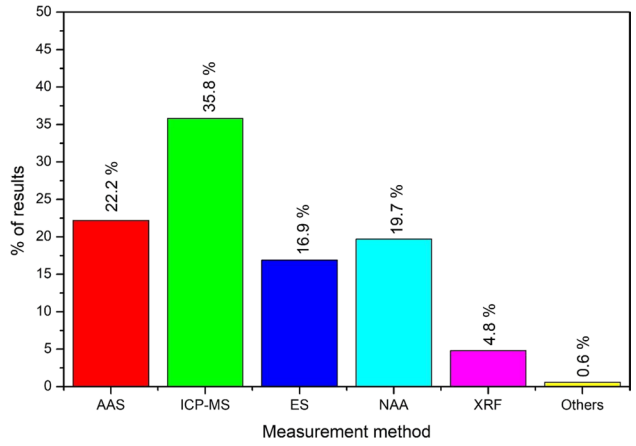

Fig. 4 The share of analytical techniques used in the certification process of M–4 CormTis

analysis (NAA), and emission spectroscopy (ES). Among them, ICP-MS distinctly prevails, what is the effect of its constant and dynamic development observed since the new millennium. The contribution of individual analytical techniques to the certification process and its evolution as a function of time was discussed in the literature (Dybczyński et al. 2003) and deserves a profound reflection. As follows from a recent review encompassing the time span of 40 years, in the years 1975–1980, the NAA was a dominating technique and its share was in the range of 40–66% (Dybczyński 2019). AAS occupied the second place followed by X-ray fluorescence (XRF), and ES. The contribution of the mass spectrometry at that time was minor or negligible. This trend was continued in the nineties although the prevalence of NAA became smaller (30–43%). At the end of the century, AAS became the technique most frequently used, followed by NAA and ICP-MS already showed its presence. In the first decade of the twenty-first century, four methods i.e. ICP-MS, NAA, ES, and AAS had almost equal share (23–25%) with marginal contribution from other methods (Samczyński *et.al.* 2012). Less than a decade later, the prevalence of ICP-MS is already clearly visible, similarly, as the further decline of the use of NAA (*cf.* Figure 4). If this trend will continue, it may lead to monopoly of ICP-MS and unavailability of NAA in the near future. The ICP-MS is an excellent method but as in the case of any other method, the systematic errors may occur for certain element–matrix combinations. The examples are e.g. the determination of scandium in INCT-TL-1 CRM (Tea leaves) (Dybczyński et al. 2017) and determination of iron in INCT-OBTL-5 CRM (Oriental Basma tobacco leaves) (Dybczyński et al., 2012). On the other hand, NAA is a nuclear method, less sensitive to matrix effects than the other methods of inorganic trace analysis, and at the same time, NAA is the only method that is essentially free from blank problems. Definitive methods by RNAA can be an addendum or alternative to IDMS as the methods of the highest metrological quality in the inorganic trace analysis. ICP-MS and NAA complement each other. It would be a pity if NAA would disappear or be unavailable in future certification campaigns. So, as was recently stated:"It should be in the interest of the whole scientific community, not only radioanalytical chemists, to keep this method alive still for many years to come" (Dybczyński 2019).

Conclusions

The new materials described in this paper extend the number of available CRMs of biological origin by two new species of sea fish tissue and one of bird tissue, respectively. The general rule for the use of CRMs is that the reference material should possibly closely mimic the samples being analyzed routinely, both with respect to matrix composition and to the mass fraction level(s) of the analyte(s). So, the new CRMs should be of interest to numerous researchers engaged in the study on the content of trace elements in food, environmental, and biomedical samples. The important scientific novelty of this work is the simultaneous use of a large number of ratio primary reference measurement procedures RPRMP (definitive methods) for independent confirmation and validation of certified values for nine essential or toxic trace elements. Very good agreement between the certified values assigned in this study and the results obtained by definitive methods for these elements, indirectly confirms also the validity and traceability of other certified values established by our standard certification procedure.

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Declarations

Ethics Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Informed consent not applicable.

Conflict of Interest Halina Polkowska-Motrenko declares that she has no conflict of interest. Zbigniew Samczyński declares that she has no conflict of interest. Rajmund S. Dybczyński declares that he has no conflict of interest. Ewelina Chajduk declares that she has no conflict of interest. Bożena Danko declares that she has no conflict of interest. Paweł Kalbarczyk declares that he has no conflict of interest. Agnieszka A. Krata declares that she has no conflict of interest. Marta Pyszynska declares that she has no conflict of interest. Iga Zuba declares that she has no conflict of interest.

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