CONSORTIUM “MODAS”

Narodowe Centrum Badań i Rozwoju
POLITECHNIKA GDAŃSKA
UNIWERSYTET WARSZAWSKI
POLITECHNIKA WARSZAWSKA
Politechnika Wrocławska

POLISH CERTIFIED REFERENCE MATERIAL (CRM)

FOR MULTIELEMENT TRACE ANALYSIS WITH INFORMATION VALUES FOR SOME PCBs AND PAHs

MODAS–5 Cod Tissue (M–5 CodTis)

GENERAL INFORMATION

INTENDED USE:	CHECKING THE ACCURACY, VALIDATION OF THE METHODS, CALIBRATION OF APPARATUS, CHECKING THE PERFORMANCE OF ANALYTICAL LABORATORIES
ELEMENTS WITH CERTIFIED VALUES:	As, Ba, Br, Cl, Cs, Cu, Fe, Hg, K, Mg, Mn, Na, P, Rb, S, Se, Sr, Zn
ELEMENTS WITH INFORMATION VALUES:	Bi, Ca, Cd, Co, Cr, Li, Ni, Pb
ANALYTES WITH INFORMATION VALUES OF CONCENTRATION:	PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, PCB-180, Pyrene, Benzo(a)pyrene, Benzo(b)fluoranthene, Bezo(k)fluoranthene, Benzo(a)anthracene, Indeno(1,2,3-cd)pyrene

Certified within the scope of "MODAS" consortium in the:

Institute of Nuclear Chemistry and Technology, Warsaw, POLAND, by the staff of Laboratory of Nuclear Analytical Methods under the direction of dr hab. Halina Polkowska-Motrenko, prof. IChTJ (inorganic trace analysis)

POLITECHNIKA GDAŃSKA

Faculty of Chemistry, Gdańsk University of Technology, Gdańsk, POLAND, by the staff of Department of Analytical Chemistry under the direction of Prof. Piotr Konieczka (PCBs and PAHs)

ORIGIN, PREPARATION AND TESTING

Cod tissue originating from fishes from Baltic Sea was prepared by the Gdańsk University of Technology. After lyophilization and grinding the material was sieved through the 200 µm sieve. Homogenization was performed in the Institute of Nuclear Chemistry and Technology, INCT (IChTJ). The whole lot of the material (ca. 60 kg) was placed in a 110 dm^3 polyethylene (PE) drum and mixed by rotating in three directions for 16 hours. The homogenized material was distributed in 50 g portions to 100 cm^3 amber glass bottles with a screw cap (future MODAS–5 Cod Tissue (M–5 CodTis) certified reference material) and in 10 g portions to 60 cm^3 bottles (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–5 CodTis were sterilized by electron beam radiation (energy 13 MeV) from a linear accelerator LAEA-13. The dose amounted to approximately 27 kGy. All operations were performed taking care to minimize any possibility of the contamination of the future CRM.

Final homogeneity checking of M–5 CodTis was done using inductively coupled plasma mass spectrometry (ICP-MS). Statistical evaluation of results for Cu, Fe, Mn, Sr, V and Zn with the use of analysis of variance (ANOVA), proved good homogeneity of the material for samples with sample mass ≥ 100 mg. Standard uncertainty due to inhomogeneity was also established. Long-term stability of the material was checked by comparing results obtained for samples stored under controlled conditions: in the air-conditioned room at 20 °C (normal storage). Samples of the CRM (ca. 250 mg) were taken from the randomly chosen bottle after 0, 2, 4, 6, 10, 12, and 15 months of storage and concentrations of As, Cu, Fe, Li, Mg, Mn, Se, Sr and Zn were determined by ICP-MS. Statistical evaluation of results did not reveal any tendency of instability in the elapsed time. Standard uncertainty associated with the long-time stability was established. Long time stability will be monitored during further storage of M–5 CodTis. Short-time stability (associated with transport) was also studied and was shown to be negligible.

Determination of moisture content

In order to express the concentrations of elements on a dry-mass basis, moisture content should be determined on a separate subsample (not that taken for analysis) by drying at 85 °C for 48 hours.

CERTIFICATION

Assigning of certified values was done on the basis of world-wide interlaboratory comparison in which 49 laboratories from 10 countries participated providing 505 laboratory averages (2367 individual determinations) for 62 elements. Their cooperation is gratefully acknowledged. From the obtained results a database was created which was subsequently subjected to statistical evaluation according to the method published previously [1] with some later modifications [2-5]. This approach is based on the outlier's rejection procedure, which uses concurrently four statistical criteria, namely those of Dixon (D), Grubbs (G), Skewness (S) and Kurtosis (K) at α = 0.05, followed by calculation of overall means of results (remaining after the outlier rejection), standard deviations, standard errors, confidence intervals etc.

The criteria used to decide whether the overall mean can be given the status of the certified value were as follows:

1. The ratio of the one-sided confidence interval and the overall mean:

$$\frac{\mathrm{SD}\cdot t_{0.05}}{\overline{X}\cdot\sqrt{N}}\quad\begin{cases}\le 20\%\ (\text{trace elements})\\ \le 10\%\ (\text{major elements})\end{cases}$$

or relative standard deviation:

$$\frac{\mathrm{SD}}{\overline{X}}\quad\begin{cases}\le 25\%\ (\text{trace elements})\\ \le 15\%\ (\text{major elements})\end{cases}$$

For the purpose of this work, elements with concentration exceeding 5000 mg kg^{-1} (ppm) were considered to be the major elements.

2. The overall mean was calculated on the basis of at least four "accepted" laboratory means (N ≥ 4) obtained by more than one analytical technique. If results from only one analytical technique are available, the number of "accepted" laboratory averages used for the calculation of the overall mean cannot be smaller than five (N ≥ 5).

3. If the conditions (1) and (2) are fulfilled but the number of outliers exceeds 50%, the additional procedure is activated which repeats the process of outlier rejection from the beginning, checking simultaneously the changes of the mean and standard deviation accompanying successive rejections. The process of rejecting of outliers is then stopped when the successive change in both the mean and standard deviation becomes lower or equal to 15%. The condition (1) is then rechecked.

4. If the above criteria are met but there are indications that after outlier rejection performed on the whole population, the remaining populations of results obtained by various analytical techniques differ significantly, the assignment of certified value is suspended and its status is described as "information" only.

"Information" values were assigned to those elements for which the results while not fulfilling simultaneously the conditions (1) (4) still fulfilled the following condition:

$$\frac{\mathrm{SD}\cdot t_{0.05}}{\overline{X}\cdot\sqrt{N}}\quad\begin{cases}\le 50\%\ (\text{trace elements})\\ \le 30\%\ (\text{major elements})\end{cases}$$

calculated on the basis of at least three "accepted" laboratory averages, and are quoted as numbers on-ly, i.e. without confidence intervals. The elements for which the data did not fulfill the above criterion were considered to be outside of any classification. In the case of some elements (As, Co, Fe, Se), the correctness of certification was additionally confirmed by definitive methods (primary reference measurement procedures) based on radiochemical neutron activation analysis (RNAA) [6-8] and in the case of Hg by isotope dilution mass spectrometry (IDMS)) [9, 10]. Traceability to SI system was maintained because the laboratories along with the analysis of M–5 CodTis analyzed also CRMs of similar matrix.

According to recent trends and recommendations to CRM producers, in addition to analytical uncertainties also the uncertainty due to the long- and short-term stability, moisture determination and inhomogeneity are taken into account. Short-term stability was shown to be negligible, so the combined standard uncertainty of the certified value u_c consists of four contributions:

$$u_c = \sqrt{u^2_{interlab} + u^2_{lstab} + u^2_{inhom} + u^2_m}$$

where $u_{interlab}$ is estimated as 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 homogeneity studies and u_m the standard uncertainty due to moisture determination. The expanded uncertainty (U), corresponding to 95% confidence level, is obtained by multiplying u_c by a coverage factor $k = t_{0.05}$ (t-Student's parameter for $\alpha = 0.05$ and $n - 1$ degrees of freedom, where n is the number of accepted laboratory averages).

CERTIFIED VALUES FOR M–5 CodTis

Macroconstituents

Element	Concentr. wt%
Cl	0.38 ± 0.11
K	1.93 ± 0.12
Mg	0.12 ± 0.02
Na	0.34 ± 0.02
P	0.96 ± 0.12
S	1.05 ± 0.16

Trace elements

Element	Concentr. mg kg^{-1}	Element	Concentr. ng g^{-1}
As	1.64 ± 0.27	Ba	162 ± 28
Br	24.8 ± 3.9	Cs	59 ± 5
Cu	1.38 ± 0.09	Hg	310 ± 22
Fe	13.2 ± 1.1	Mn	921 ± 75
Rb	4.54 ± 0.33		
Se	1.33 ± 0.10		
Sr	4.07 ± 0.36		
Zn	20.1 ± 1.1		

INFORMATION VALUES FOR M–5 CodTis

Bi	7 ng g^{-1}
Ca	0.11 wt %
Cd	5 ng g^{-1}
Co	14 ng g^{-1}
Cr	201 ng g^{-1}
Li	26 ng g^{-1}
Ni	136 ng g^{-1}
Pb	45 ng g^{-1}

Storage conditions and stability

MODAS-5 Cod Tissue (M–5 CodTis) should be stored at room temperature in the dark in the tightly closed bottle. In these conditions its shelf life is valid until Dec. 31, 2020.

Note: the guarantee of stability is valid for the material stored in the original closed bottle in the conditions as specified above.

Warsaw, May, 2015

LITERATURA

1. R. Dybczyński, Anal. Chim. Acta, 117 (1980) 53-70.
2. R. Dybczyński, H. Polkowska-Motrenko, Z. Samczyński, Z. Szopa, Geostandards Newsletter, 15 (1991) 163-185.
3. Z. Szopa, J. Jaszczuk, R. Dybczyński, Nukleonika, 41 (1996) 117-127.
4. R. Dybczyński, B. Danko, K. Kulisa, E. Maleszewska, H. Polkowska-Motrenko, Z. Samczyński, Z. Szopa, Chem. Anal. (Warsaw), 49 (2004) 143-158.
5. H. Polkowska-Motrenko, R.S. Dybczyński, E. Chajduk, Accred. Qual. Assur., 15 (2010) 245-259.
6. R. Dybczyński, B. Danko, J. Radioanal. Nucl. Chem., 181 (1994) 43-49.
7 R. Dybczyński, B. Danko, H. Polkowska-Motrenko, Z. Samczyński, Talanta, 71 (2007) 529-536.
8. R.S. Dybczyński, H. Polkowska-Motrenko, E. Chajduk, B. Danko, M. Pyszynska, J. Radioanal. Nucl. Chem., 302 (2014) 1295-1302.
9. A. Krata, B. Ari B, C. Quetel, "Isotope Dilution Inductively Coupled Plasma Mass Spectrometry applied for establishment of reference value of the total Hg content in a mineral feed test material for IMEP-111", European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Geel, Belgium, JRC62101, 2010.
10. L. Fischer, M. Brunner, T. Prohaska, S. Hann, J. Anal. At. Spectrom., 27 (2012) 1983-1991.

LISTA UCZESTNIKÓW PORÓWNANIA MIĘDZYLABORATORYJNEGO M–5 CodTis

(w porządku alfabetycznym)

Prof. Dr. hab. D. Barałkiewicz, Uniwersytet im. Adama Mickiewicza, Poznań, POLAND;
Dr. A. Bielicka-Giełdoń, Uniwersytet Gdański, Gdańsk, POLAND;
Prof. Dr. hab. M.H. Borawska, Dr. hab. K. Socha, Dr. J. Soroczyńska, Uniwersytet Medyczny w Białymstoku, POLAND;
Prof. Dr. hab. E. Bulska, Dr. A. Krata, Dr. A. Ruszczyńska, Mrs. A. Łuciuk, Uniwersytet Warszawski, Warszawa, POLAND;
Dr. Y. Bychkova, Laboratory of Mineral Substance Analysis IGEM RAS, Moscow, RUSSIA;
Prof. Dr. hab. inż. K. Chojnacka, **Politechnika Wrocławska, Wrocław, POLAND;**
Dr. E. Chuparina, Vinogradov Institute of Geochemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk, RUSSIA;
Mr. M. Cibor, Wessling Polska Sp. z o.o., Kraków, POLAND;
Mrs. M. Drewnowska, Mrs. A.K. Kojta, Uniwersytet Gdański, Gdańsk, POLAND;
Mr. B. Ermolaev, Mrs. G. Granovskay, Mrs. O. Okina, Geological Institute of Russian Academy of Sciences, Moscow, RUSSIA;
Mrs. A. Florek, Hamilton Poland S.A., Gdynia, POLAND;
Prof. Dr. hab B. Godlewska-Żyłkiewicz, Uniwersytet w Białymstoku, Białystok, POLAND;
Mr. A. Jaklewicz, Dr. M. Kuras, Warszawski Uniwersytet Medyczny, Warszawa, POLAND;
Dr. R. Jasan, Dr. S. Resnizky, Mrs. R. Plá, Argentine National Atomic Energy Commission, Buenos Aires, ARGENTINA;
Prof. Dr. hab. R. Jędrzejczak, Instytut Biotechnologii Przemysłu Rolno-Spożywczego, Warszawa, POLAND;
Dr. V.K. Karandashev, Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences, Moscow, RUSSIA;
Mrs. D. Karmasz, Mrs. E. Górecka, Mrs. E. Kaływa, Mr. J. Retka, Mr. J. Kucharzyk, Mrs. W. Bureć-Drewniak, Państwowy Instytut Geologiczny, Centralne Laboratorium Chemiczne, Warszawa, POLAND;
Mrs. D. Kolasa, Mrs. A. Bajszczak, Mrs. J. Dłubak, Prof. Dr. hab. A. Czerwiński, Dr. Z. Rogulski, Instytut Chemii Przemysłowej, Warszawa, POLAND;
Prof. Dr. V.P. Kolotov, Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences, Moscow, RUSSIA;
Prof. Dr. hab. inż. P. Konieczka, Mrs. inż. K. Dubalska, Mrs. M. Rutkowska, Politechnika Gdańska, Gdańsk, POLAND;
Dr. W. Korol, Instytut Zootechniki, Krajowe Laboratorium Pasz, Lublin, POLAND;
Mrs. M. Kozłowska, Wojewódzka Stacja Sanitarno-Epidemiologiczna w Szczecinie, POLAND;
Mrs. J. Krzywicka, Wojewódzki Inspektorat Ochrony Środowiska w Białymstoku, Delegatura w Suwałkach, POLAND;
Mr. S. Lierhagen, Norwegian University of Science and Technology, Trondheim, NORWAY;
Dr. V.A. Maihara, Instituto de Pesquisas Energéticas e Nucleares- IPEN/CNEN, Sao Paulo, BRAZIL;
Dr. M. Mania, Narodowy Instytut Zdrowia Publicznego – Państwowy Zakład Higieny, Warszawa, POLAND;
Mr. J. Markowski, Instytut Zootechniki, Krajowe Laboratorium Pasz, Szczecin, POLAND;
Dr. V. G. Merkulov, Tomsk Polytechnic University Tomsk, RUSSIA;
Dr. B. Mikuła, Dr. A. Kita, Dr. B. Feist, Uniwersytet Śląski, Katowice, POLAND;
Mr. J. Ostrowski, Instytut Nawozów Sztucznych, Puławy, POLAND;
Dr. V. I. Otmahov, Tomsk Polytechnic University, Tomsk, RUSSIA;

Mr. A. Pastorelli, National Reference Laboratory, Rome, ITALY;
Dr. A. Pawlaczyk, Dr. hab. M.I. Szynkowska, Politechnika Łódzka, Łódź, POLAND;
Mr. Z. Polański, ARSO Polański Sp. z o.o., Baniocha k/Warszawy, POLAND;
Mr. K. Rajczykowski, Mrs. K. Widziewicz, Dr. hab. inż. K. Loska, Dr. hab. inż. I. Korus, Politechnika Śląska, Gliwice, POLAND;
Dr. inż. M. Rajkowska-Myśliwiec, Zachodniopomorski Uniwersytet Technologiczny, Szczecin, POLAND;
Mrs. J. Sacharewicz, Wojewódzki Inspektorat Ochrony Środowiska Białystok, POLAND;
Dr. inż. Z. Samczyński, Dr. B. Danko, Mrs. I. Kużelewska, Instytut Chemii i Techniki Jądrowej, Warszawa, POLAND;
Prof. Dr. M. Santoso, Center of Nuclear and Science Technology Application, National Nuclear Energy Agency, Bandung, INDONESIA;
Mrs. K. Skarupska, Wojewódzki Inspektorat Ochrony Środowiska w Zielonej Górze, POLAND;
Dr. A. Sorbo, Dr. M. Ciprotti, Dr. A.C. Turco, European Union Reference Laboratory for Chemical Elements in Food of An-imal Origin, Rome, ITALY;
Prof. Dr. hab. I. Staneczko-Baranowska, Dr. inż. B. Kowalski, Politechnika Śląska, Gliwice; POLAND;
Dr. J.H. Sterba, Vienna University of Technology, Vienna, AUSTRIA;
Mrs. N. Todorova, Central Laboratory of Veterinary Control and Ecology, Sofia, BULGARIA;
Mrs. M. Turkowska, Instytut Nawozów Sztucznych, Gliwice, POLAND;
Dr. H. Uggerud, Norwegian Institute for Air Research, Kjeller, NORWAY;
Dr. S. Waheed and Dr. N. Siddique, Pakistan Institute of Nuclear Science and Technology, Islamabad, PAKISTAN;
Dr. inż. M. Wełna, Dr. inż. A. Leśniewicz, Dr. inż. A. Szymczycha-Madeja, Dr. inż. J. Borkowska-Burnecka, Prof. Dr. P. Pohl, Politechnika Wrocławska, Wrocław, POLAND.

PCBs and PAHs – information values

CERTIFICATION

Among the 11 laboratories that participated in the certification campaign, only the small group has sent the results of the determinations of PCBs and PAHS in tissue samples. In this connection, that the maximum number of results does not exceed the 5, values of concentrations of PAHs and PCBs have been presented as the information values.

Measurement traceability

The measurement traceability to SI units has been achieved by the use of analytical balances and weights related to national measurement standards, certified standard solution for calibration of measurement equipments and CRMs traceable to SI units.

INFORMATION VALUES (RANGES OF RESULTS) FOR M–5 CodTis

ANALYTE	INFORMATION VALUE	NUMBER OF RESULTS
PCB-28	0.31 µg/kg (0.20-0.45) µg/kg	3
PCB-52	0.21 µg/kg (0.19-0.25) µg/kg	3
PCB-101	0.49 µg/kg (0.19-0.76) µg/kg	3
PCB-118	2.0 µg/kg (0.70-3.8) µg/kg	3
PCB-138	3.4 µg/kg (0.27-7.2) µg/kg	4
PCB-153	4.2 µg/kg (0.27-11) µg/kg	4

ANALYTE	INFORMATION VALUE	NUMBER OF RESULTS
PCB-180	0.94 µg/kg (0.40-2.1) µg/kg	3
Pyrene	1.2 µg/kg (0.27-2.5) µg/kg	4
Benzo(a)pyrene	1.4 µg/kg (0.27-2.7) µg/kg	4
Benzo(b)fluoranthene	1.2 µg/kg (0.03-3.0) µg/kg	5
Benzo(k)fluoranthene	1.6 µg/kg (0.04-3.9) µg/kg	4
Benzo(a)anthracene	0.69 µg/kg (0.06-1.5) µg/kg	4
Indeno (1,2,3-cd)pyrene	2.7 µg/kg (0.34-5.0) µg/kg	4

Storage conditions and stability

MODAS M–5 CodTis should be stored at room temperature, protected from light in firmly closed container. In such conditions, the shelf life of the M–5 CodTis has been established to be 31 December 2020.
Long-time stability is monitored during storage.
Note: Guarantee refers to the storage of the material under the above specified conditions in a container closed by the manufacturer.

Gdańsk, May, 2015

LIST OF PARTICIPANTS OF THE INTERCOMPARISON M–5 CodTis

(in alphabetical order)

Mgr Paulina Chaber, CentLab Instytutu Ochrony Środowiska – Państwowego Instytutu Badawczego, Warsaw, POLAND
Prof. dr hab. B. Buszewski, Dr hab. T. Kowalkowski, Dr hab. Renata Gadzała-Kopciuch, Mgr Anna Kiełbasa, Mgr Iwona Krzemień-Konieczka, UMK Toruń, POLAND
Dr inż. Katarzyna Galer-Tatarowicz, Zakład Ochrony Środowiska Instytutu Morskiego w Gdańsku, Gdańsk, POLAND
Dr hab. inż. Adam Grochowalski, Laboratorium Analiz Śladowych Politechniki Krakowskiej, Krakow, POLAND
Mgr Jadwiga Krzywicka, WIOŚ Białystok, Pracownia w Suwałkach, Suwałki, POLAND
Dr Alina Marcinkowska, Mgr Anna Konstanciuk, J. S. Hamilton S.A., Gdynia, POLAND
Dr hab. inż. Bożena Zabiegała, Dr inż. Marta Słomińska, Dr inż. Mariusz Marć, Katedra Chemii Analitycznej, Wydział Chemiczny, Politechnika Gdańska, Gdańsk, POLAND

Narodowe Centrum
Badań i Rozwoju

Realizacja projektu dofinansowana przez Narodowe Centrum Badań i Rozwoju.
Nr umowy: INNOTECH-K1/IN1/43/158947/NCBR/12