Please read the whole text below before starting the analysis

COLLABORATIVE STUDY ON THE DETERMINATION OF TRACE ELEMENTS IN FOUR CANDIDATE REFERENCE MATERIALS:

MODAS-2 Bottom Sediment **(M-2 BotSed),**
MODAS-3 Herring Tissue **(M-3 HerTis),**
MODAS-4 Cormorant Tissue **(M-4 CormTis),**
MODAS-5 Cod Tissue **(M-5 CodTis)**

General information

The general objective of this project is preparation of four new certified reference materials (CRMs). The aim of the collaborative study is to collect sufficiently great number of analytical results from participating laboratories using various analytical techniques. This set of data will be the basis for assigning certified and information values in the candidate reference materials.

Another important purpose is enabling the participating laboratories to check their analytical performance by comparing own results with those from other participants as well as with the finally established certified and/or information values.

The participants are expected to analyze all or some of the four materials enclosed, using the method(s) of their choice and report the results in mg kg^{-1} dry mass *(ppm)* as described in the section "Reporting of results". To secure anonymity the participants will be coded, the code being known only to them and to the organizers.

The deadline for returning the results is ***April 15, 2014.***

After completing the collaborative study, evaluation of results and assigning certified and information values, the participants will receive complimentary 50 g sample(s) of CRM(s) to the certification of which they have contributed.

Description of materials

MODAS-2 Bottom Sediment (M-2 BotSed)

The material originating from the bottom of the Vistula River nearby Włocławek (Poland) was prepared by the Nicolaus Copernicus University in Toruń. After collecting and freeze-drying, it was sieved through a 100 μm sieve.

The next step was homogenization performed by the Institute of Nuclear Chemistry and Technology (INTC). The whole lot of bottom sediment powder was transferred to a 110 dm^3 PE drum and homogenized by mixing for 16 hours in a homogenizer rotated in three directions assuring good mixing of the content.

The material was then distributed into 100 cm^3 amber glass bottles with a screw cap in 50 g portions (future CRM) and in 10 g portions into 60 cm^3 amber glass bottles (intercomparison samples).

In order to ensure the long-term stability of the new CRM, all containers with M-2 BotSed were sterilized at INCT by electron beam radiation (energy 13 MeV) from a linear accelerator LAEA-13. The dose amounted to approximately 27 kGy.

All the above operations were performed in a way eliminating as much as possible the potential contamination of the material with metals.

Final homogeneity checking was accomplished by inductively coupled plasma-mass spectrometry (ICP-MS). Statistical evaluation of analytical results employing the analysis of variance (ANOVA) proved good homogeneity of the material for sample mass at least 100 mg.

MODAS-3 Herring Tissue (M-3 HerTis)

The material originating from the Nord See was prepared by the Gdańsk University of Technology. After freeze-drying and grinding, it was sieved through a 200 μm sieve.

Homogenization, distribution (into 100 cm^3 and 60 cm^3 glass amber bottles, accordingly), radiation sterilization as well as homogeneity checking were performed at INTC in the same manner as above.

MODAS-3 Herring Tissue can be considered as homogeneous at least for sample mass ≥ 100 mg.

MODAS-4 Cormorant Tissue **(M-4 CormTis)**

The material originating from Czech Republic was prepared by the Gdańsk University of Technology. After freeze-drying and grinding, it was sieved through a 200 μm sieve.

Homogenization, distribution (into 100 cm^3 and 60 cm^3 glass bottles, accordingly), radiation, sterilization as well as homogeneity checking were performed at INTC in the same manner like in the case of the first material.

MODAS-4 Cormorant Tissue can be considered as homogeneous at least for sample mass ≥ 100 mg.

MODAS-5 Cod Tissue **(M-5 CodTis)**

The material originating from the Baltic See was prepared by the Gdańsk University of Technology. After freeze-drying and grinding, it was sieved through a 200 μm sieve.

Homogenization, distribution (into 250 cm^3 and 60 cm^3 glass bottles, accordingly), radiation, sterilization as well as homogeneity checking were performed at INTC in the same manner like in the case of the first material.

MODAS-5 Cod Tissue can be considered as homogeneous at least for sample mass ≥ 100 mg.

Determination of moisture content

The following conditions were established for the determination of dry mass in the candidate reference materials:

- **M-2 BotSed – by drying a separate sample (approx. 200–400 mg) at 105°C for 24 hours,**
- **M-3 HerTis – by drying a separate sample (approx. 200–400 mg) at 85°C for 48 hours,**
- **M-4 CormTis – by drying a separate sample (approx. 200–400 mg) at 85°C for 48 hours,**
- **M-5 CodTis – by drying separate sample (approx. 200–400 mg) at 85°C for 48 hours.**

The moisture contents as determined in our laboratory amounted to 3.0 % for M-2 BotSed, 5.9 % for M-3 HerTis, 4.5 % for M-4 CormTis, and 4.1 % for M-5 CodTis.

The moisture content may vary quite considerably with the changes in the ambient humidity and temperature. Every participant is requested to make his own determinations of moisture contents of the four materials in the same conditions as described above. Weighing of subsamples for moisture determination should be done parallel to weighing subsamples taken for analysis. All results for the determination of elements in the analyzed materials should be reported on a dry mass basis. The dry mass m_{dry}, of a material can be obtained from the mass of material (as received) taken for analysis $m_{as\ received}$, from the formula:

$$m_{dry} = \frac{m_{as\ received}(100 - \%\ H_2O)}{100}$$

where % H_2O is percent moisture content determined as described above.

Reporting of results

The participants are requested to determine as many elements as they can from the list shown in the **MODAS - Analytical Results.xls (As, Ba, Cd, Co, Cr, Cs, Cu, Eu, Fe, Hf, Hg, I, La, Mo, Mn, Ni, Pb, Sb, Sc, Se, Sm, Sn, Sr, Tb, Th, U, Zn)**. However, the results for any other elements are also welcome. It is requested to make at least **three** but preferably **six** separate determinations for each analyte and report the results electronically in the MS Excel file (sent by E-mail) **MODAS - Analytical Results.xls**, consisting of four sheets. Each sheet is intended for the separate candidate reference material i.e. *MODAS-2 Bottom Sediment* (M-2 BotSed), *MODAS-3 Herring Tissue* (M-3 HerTis), *MODAS-4 Cormorant Tissue* (M-4 CormTis), *MODAS-5 Cod Tissue* (M-5 CodTis) and analytical results should be reported accordingly.

The concentrations should be entered as net values (i.e. after correcting for blank, moisture etc.) and expressed in mg kg^{-1} dry mass (ppm) using as many

significant figures as it is justified by the accuracy of the method employed. Exponential way of expressing numbers can be used in the case of need. Apart from the determined concentration values for a given element, the participants are also requested to give the following data:

1. **The average mass of the analyzed sample (in mg),**
2. **The detection limit of the method used (in mg kg^{-1}),**
3. **The combined standard uncertainty of the measurement (in %),**
4. **The symbol of the quantitative determination technique applied (e.g. AAS, ES, ICP-MS, NAA etc.).**

The MS Word file **MODAS - Report Form.doc** is intended to report short description of the whole analytical procedure performed and will be sent to the participating laboratories by E-mail. Particular row corresponds to the given material. The following information should be written:

- Sample pretreatment,
- Preconcentration and separation procedure (if any)
- Technique of quantitative determination,
- Certified reference material(s) used for the quality control.