VALUE ASSIGNMENT FOR A BRAZILIAN MUSSEL REFERENCE MATERIAL

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In a previous communication the output of an interlaboratory comparison for the determination of mass fractions and corresponding characterization standard uncertainties (u_{char}) of 36 elements in a *Perna perna* mussel reference material produced in Brazil was presented [1]. The mass fractions were determined by seventeen laboratories using eleven measurement methods. The objective of the present study was to assign element mass fraction values to the mussel reference material taking into account not only u_{char} but also the standard uncertainty contributions due to the between bottle homogeneity (u_{bb}), long-term stability (u_{lts}) and short-term stability (u_{sts}) to the mass fraction combined standard uncertainties (u_{CRM}) in order to comply with ISO Guide 35 guidelines to the certification of reference materials [2].

The assessment of the uncertainty components was performed on data of the homogeneity and stability studies which were previously carried out on the mussel reference material. The u_{bb} was estimated from the output of the analysis of variance tests performed in the homogeneity study with six bottles and eight replicate determinations. The u_{sts} was considered negligible in this study as the material proved to be stable for normal transport conditions in the short-term stability study performed. The u_{lts} was calculated from the angular coefficient of the linear regression curve of mass fraction as a function of time from the long-term stability study, considering a two-year shelf life period.

Table 1 presents the assigned mass fraction values and associated expanded uncertainties as well as the various contributions to the combined uncertainty. It was observed that the residual non homogeneity of the batch of the material was the lowest contribution to u_{CRM} while the contribution due to the long-term stability was the highest for most elements, even for a relatively short shelf life period. Possibly the ISO Guide 35 approach used provided overestimated u_{lts} results, considering that freeze-dried biological materials of marine origin are usually certified for longer shelf life periods.

In this study, the criteria for the classification of the assigned values for the certification of the mussel reference material were:

- Certified values: values obtained by 4 or more laboratories, using measurement methods with at least 2 measurement principles and with relative expanded uncertainties below 20%;
- Reference values: values obtained by 4 or more laboratories, but with only one measurement principle and/or with expanded uncertainties above 20%;
- Informative values: values obtained by less than 4 laboratories.

Table 1. MASS FRACTIONS IN MG KG^{-1} (ROBUST MEANS AND EXPANDED UNCERTAINTIES, K = 2) AT DRY MASS BASIS OBTAINED IN THE INTERLABORATORY COMPARISON FOR THE CHARACTERIZATION OF THE *PERNA PERNA* MUSSEL REFERENCE MATERIAL AND CORRESPONDING CONTRIBUTIONS TO THE COMBINED STANDARD UNCERTAINTIES (U_{CRM})

Element	Standard uncertainty component				Mass fraction, mg kg^{-1}	U, %
	u_{char}	u_{bb}	u_{lts}	u_{CRM}		
Ag	0.11	0.081	0.15	0.21	2.45 ± 0.41	17
Al, g kg^{-1}	0.062	0.024	0.059	0.089	1.19 ± 0.18	15
As	0.27	0.12	0.82	0.87	13.6 ± 1.7	13
Br	8.6	2.9	19	21	248 ± 42	17
Ca, g kg^{-1}	0.043	0.054	0.14	0.15	2.72 ± 0.31	11
Cd	0.050	0.0047	0.011	0.051	0.58 ± 0.10	18
Ce	0.049	0.036	0.091	0.11	1.82 ± 0.22	12
Cl, g kg^{-1}	0.79	0.92	1.8	2.2	36.9 ± 4.4	12
Co	0.016	0.0031	0.035	0.038	0.829 ± 0.077	9.3
Cr	0.055	0.0087	0.13	0.14	1.24 ± 0.28	22
Cs	0.0025	0.0011	0.013	0.013	0.106 ± 0.026	25
Cu	0.27	0.23	0.56	0.67	11.3 ± 1.3	12
Eu	0.0024	0.00021	0.0035	0.0042	0.0291 ± 0.0084	29
Fe	12	4.6	23	27	593 ± 53	9.0
Hf	0.0013	0.00082	0.0021	0.0026	0.0411 ± 0.0051	13
Hg	0.011	0.0018	0.018	0.021	0.165 ± 0.041	25
I	0.52	0.26	0.64	0.86	12.9 ± 1.7	13
K, g kg^{-1}	0.25	0.14	0.41	0.50	8.2 ± 1.0	12
La	0.030	0.0063	0.062	0.069	0.82 ± 0.14	17
Mg, g kg^{-1}	0.087	0.034	0.19	0.21	3.73 ± 0.42	11
Mn	0.84	0.47	1.1	1.5	22.7 ± 3.0	13
Na, g kg^{-1}	0.53	0.220	1.72	1.81	22.8 ± 3.6	16
Ni	0.46	0.14	0.35	0.59	7.0 ± 1.2	17
P, g kg^{-1}	0.53	0.32	0.80	1.0	15.9 ± 2.0	13
Pb	0.060	0.011	0.040	0.073	0.56 ± 0.15	26
Rb	0.14	0.072	0.43	0.46	4.93 ± 0.92	19
S, g kg^{-1}	2.2	0.44	1.1	2.5	21.9 ± 5.0	23
Sc	0.0021	0.0024	0.011	0.011	0.199 ± 0.023	11
Se	0.13	0.030	0.18	0.22	4.42 ± 0.45	10
Sm	0.0032	0.0030	0.0076	0.0088	0.152 ± 0.018	12
Sr	2.4	0.68	1.7	3.1	34.0 ± 6.1	18
Th	0.0069	0.0017	0.019	0.020	0.280 ± 0.041	15
U	0.017	0.0029	0.0072	0.019	0.143 ± 0.037	26
V	0.26	0.066	0.14	0.31	2.89 ± 0.61	21
Yb	0.040	0.0055	0.014	0.042	0.273 ± 0.085	31
Zn	2.1	0.83	4.2	4.7	118.5 ± 9.5	8.0

u_{char}, standard uncertainty due to characterization; u_{bb}, standard uncertainty due to between-bottle homogeneity; u_{lts}, standard uncertainty due to long-term stability; u_{CRM}, standard uncertainty of the assigned value; U, %, relative expanded uncertainty

According to these criteria, element assigned values were classified as follows:

- Certified values for Al, As, Ca, Cd, Cl, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Se, Th and Zn;
- Reference values for Ag, Br, Ce, Cr, Cs, Eu, La, Rb, Sc and V;
- Informative values for Hf, Hg, I, P, Pb, S, Sm, Sr, U and Yb.

References

[1] MOREIRA, E.G., VASCONCELLOS, M.B.A., MAIHARA, V.A., CATHARINO, M.G.M., SAIKI, M., Interlaboratory comparison for the characterization of a Brazilian mussel reference material. Submitted for publication at Accred. Qual. Assur.

[2] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, ISO Guide 35, Reference materials – General and statistical principles for certification, ISO, Geneva (2006).

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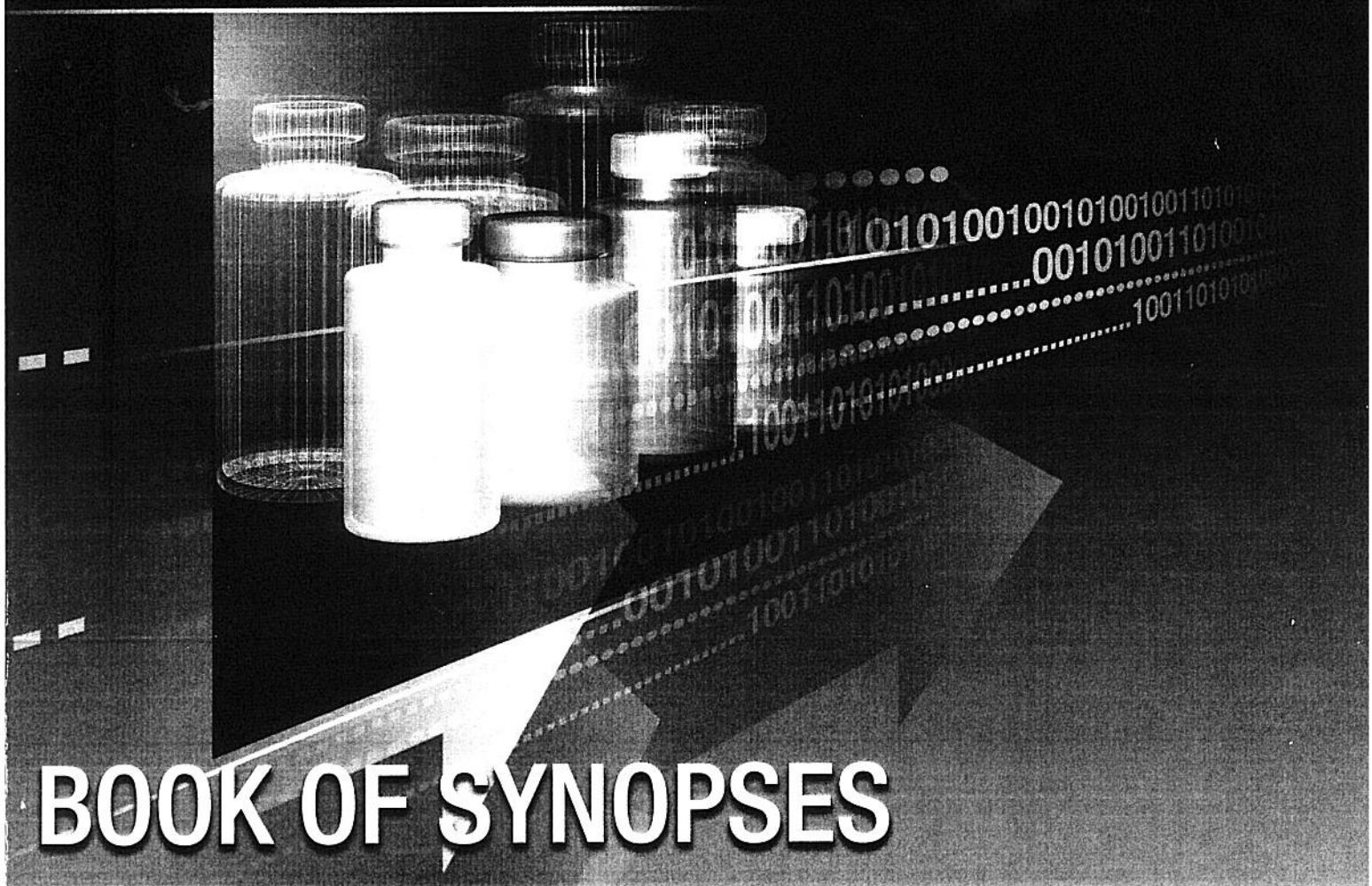

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