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Trace element quality control analysis of environmental samples at the Neutron Activation Analysis Laboratory, IPEN, São Paulo, Brazil

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As part of its Quality Assurance Program, the Neutron Activation Analysis Laboratory (LAN-IPEN) has participated of several interlaboratory comparisons, analyzing the following environmental samples: Fish Tissue (IAEA-407), Seafood Material (*Elementos en Almeja,* MR-CCHEN-02), Tea Leaves (INCT-TL-1), Mixed Polish Herbs (INCT-MPH-2) and Marine Sediment Sample (IAEA-433). Up to thirty elements were determined in the candidate reference materials by instrumental neutron activation analysis. The performance of the laboratory has been statistically evaluated (*Z*-score) in relation to assigned values calculated from all data provided by the participant laboratories. The results obtained showed, as a general trend, *Z*-score values ($|Z|<2$) for most elements showing the good quality of the analytical data for these matrices analyzed by using a nuclear analytical technique.

Introduction

Analytical laboratories have been very much concerned lately with analytical quality control. One of the main objectives of all laboratories around the world is to assure the quality and credibility of the results, allowing international acceptance and comparison of analytical data. The IPEN Neutron Activation Analysis Laboratory (LAN-IPEN) has implemented a Quality Assurance Program, which comprises among many other activities the participation in intercomparison runs, which are considered one of the standard procedures in quality assurance programs, since they help the laboratories to find out deficiencies and systematic errors in their analytical methods, improving their data. The results, in general a mean of six replicates, are sent to the organizers of the interlaboratory comparison and are statistically evaluated with all contributed data. For each element analyzed, a certified or recommended or information value is assigned, depending on the consensus of the different laboratories data. The performance of each laboratory is verified by comparing the obtained results with the certified/recommended values. In the present paper, this comparison was performed by using the *Z*-score criterion.[1] This score can be used by each laboratory to judge the accuracy of its routine determinations; "satisfactory" results should be $|Z|<2$. The elements As, Ba, Br, Ca, Cl, Co, Cr, Cs, Fe, Hf, K, Mn, Na, Rb, Sb, Sc, Se, Ta, Th, U, V, Zn and rare earths were determined in the following environmental samples: Fish Tissue (IAEA-407), Seafood Material (*Almeja Venus Antiqua,* MR-CCHEN-002), Tea Leaves (INCT-TL-1), Mixed Polish Herbs (INCT-MPH-2) and Marine Sediment Sample (IAEA-433) by instrumental neutron activation analysis (INAA).

The candidate reference materials INCT-MPH-2 and INCT-TL-1 were prepared by the Institute of Nuclear Chemistry and Technology (INCT), Poland. INCT-MPH-2 was prepared from the mixture of herbs collected in a non contaminated rural area used for drugs production and INCT-TL-1 from black tea, which is usually packed in tea bags.[2,3]

The intercomparison exercise in a marine sediment sample (IAEA-433) was organized by the International Atomic Energy Agency, Marine Environmental Studies Laboratory, Monaco. The sediment was collected in the Mediterranean Sea, off the coast of Algeria.[4]

The reference material Fish Tissue (IAEA-407) was prepared by the International Atomic Energy Agency to be used as a reference material for the measurement of trace elements and methylmercury (MeHg) in fish tissue samples. A large quantity of whole fish was collected in 1999 from the North Sea. Most of which was collected was herring, but the sample material also contained capelan and anchovy.[5]

The reference material MR-CCHEN-02, *Elementos en Almeja (Venus antiqua)*, was prepared by the Chilean Nuclear Energy Commission to be used as reference for the measurement of trace and major elements in marine biological samples. The *almejas* were collected in the bottom of a bay located in the central zone of Chile.[6]

Experimental

Two hundred mg of the samples were accurately weighed in polyethylene envelopes, previously cleaned with diluted nitric acid solution. Standards of the elements of interest were prepared by mixing appropriate aliquots of solutions of these elements made from spectroscopically pure reagents or from SPEX CERTIPREP certified standard solutions. Aliquots of

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these solutions were pipetted onto 1 cm^2 pieces of Whatman No. 40 filter paper, evaporated to dryness under an infrared lamp, and sealed in polyethylene envelopes, similar to those used in the preparation of the samples. Usually, four elements were combined into one envelope.

For the determination of V, Cl and Mn, samples and standards were irradiated for 5 minutes at a thermal neutron flux of $4 \cdot 10^{11}$ $n \cdot cm^{-2} \cdot s^{-1}$, at the IEA-R1 nuclear reactor of Instituto de Pesquisas Energéticas e Nucleares. For the other elements (As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, K, Na, Rb, Sb, Sc, Se, Ta, Th, U, Zn , and the rare earths La, Ce, Nd, Sm, Eu, Tb and Yb), samples and standards were irradiated for 8 to 16 hours at a thermal neutron flux of $1 \cdot 10^{13}$ $n \cdot cm^{-2} \cdot s^{a}1$. The measurements of the induced gamma-ray activity were carried out using a GX20190 hyperpure Ge detector. The multichannel analyzer was a 8192-channel Canberra S-100 plug-in-card in a PC computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma-ray of ^{60}Co. For the 5 minutes irradiation, decay and counting times were each 3 minutes. Two series of measurements were performed after the 8–16 hour irradiation. The first was done from 5 to 7 days after irradiation (sample-detector distance of 9 cm) and the second one after 15–20 days of decay (sample-detector distance of 3 cm). Counting times ranged from 3 to 10 hours. The gamma-ray spectra were processed by using in-house gamma-ray software, VISPECT,[7] which locates peak position and calculates the energies and net areas.

Results and discussion

The results obtained (mean and uncertainties at 95% confidence interval for six replicate analysis), as well as certified/recommended/information values and detection limits, calculated by using the CURRIE's criterion,[8] are shown in Table 1. The methodology accuracy and precision were evaluated by analyzing the certified reference material Orchard Leaves (NIST SRM1571) for the biological materials, and the geological reference materials Soil-7 (IAEA) and Buffalo River Sediment (NIST SRM2704) for the marine sediment IAEA-433. Figures 1 to 5 show the standardized difference or *Z*-score for each element in the materials analyzed. In general, the organizers of the intercomparison trials provide the results of the laboratory performance but, in fact, only for the IAEA reference materials a statistical evaluation of all the participant laboratories was performed; so, it was considered important to do it for the other reference materials. The target standard deviation (s_b) was selected considering that the laboratory should have a relative bias equal to or better than 25% (2 s_b, $s_b = 12.5\%$). As reported by WYSE et al.,[4] a fixed value of s_b has the advantage that the *Z*-scores derived from it can be compared from round to round to demonstrate general trends of the laboratory.

If $|Z|<2$, the performance is considered satisfactory showing that the relative deviation from the recommended value is equal or better than 25%. *Z*-scores from 2 to 3 indicate that the results are of questionable quality. It can be observed that for almost all elements the results obtained presented $|Z|<2$ and that the data were randomly higher or lower than certified or recommended values, showing no systematic analytical errors (Figs 1 to 5).

In INCT-MPH-2, only As and Sb presented $|Z|>2$ ($|Z| = 2.3$ and 2.1, respectively). In the case of Sb, the discrepancy may be attributed to the low concentration level of this element, close to the detection limit. For As, the error may be attributed to the interference of the 554.3 keV gamma-ray peak of ^{82}Br in the 559.1 keV peak of ^{76}As in the gamma-ray spectrum, as far as the relationship between the concentration of As and Br in this reference material is significant (1:40). The results obtained for Fe, Na and U were in good agreement with information values (Table 1).

In the analysis of INCT-TL-1 reference material, only Cr presented $|Z|>2$ ($Z = -2.3$). The results of Fe, Sb, and Se also agreed with information values (Table 1).

In the reference material Fish Tissue (IAEA-407), only Sb presented a high positive bias due to the low concentration (same magnitude order of the detection limit) and also to the interference of the 563.2 keV and 559.1 keV peaks of ^{76}As in the 564.2 keV peak of ^{122}Sb. For Marine Sediment (IEA-433), only the *Z*-scores reported in the IAEA report of the intercomparison exercise[4] are presented in Fig. 4. It can be observed that all the elements in Fig. 4 presented $|Z|<2$. The results of the other elements are shown in Table 1 and are in good agreement with recommended and information values. In the IAEA reports of the intercomparison exercises IAEA-407 and IAEA-433,[4,5] LAN-IPEN has been classified in Group 1, for laboratories with $|Z|<3$ for 90% of the data.

For *Almeja* MR-CCHEN-002, only Fe presented $|Z|>2$ ($Z = 2.6$).

The contribution of LAN-IPEN in the certification of the reference materials analyzed was very significant. LAN-IPEN has provided results for 19 elements within the 34 certified for the INCT-MPH-2 material and the 33 certified for the INCT-TL-1 material. For IAEA-407 material, all the results provided, except for Sb, were used in the certification of the material and, for IAEA-433 material, 23 of the 39 recommended values were included in the certification trial.

Table 1. Concentration of some major and trace elements in the candidate reference materials by INAA (in mg·kg^{-1})

Element	Tea Leaves INCT-TL-1		Polish Herbs INCT-MPH-2		Fish Tissue IAEA-407		Almeja MR-CCHEN-002		Detection limit	Marine Sediment IAEA-433[7]		Detection limit
	This work	Certified/information values[2]	This work	Certified/information values[3]	This work	Recommend values[4]	This work	Reference values (95% confidence level)[6]		This work	Certified/ recommended values[5]	
As	–	0.106 ± 0.021	0.24 ± 0.05	0.191 ± 0.023	13.0 ± 0.7	12.6 ± 1.2	6.3 ± 0.2	6.05 (5.88–6.22)	0.06	16.9 ± 0.3	18.9 ± 1.8	0.60
Ba	45 ± 2	43.2 ± 3.9	29 ± 1	32.5 ± 2.5	–	12.6 ± 1.2	6.5 ± 1.9	–	5	271 ± 22	268 ± 32	58
Br	13 ± 1	12.3 ± 1.0	–	7.71 ± 0.61	98 ± 3	94 ± 9	106 ± 3	104.6 (97.1–112.0)	0.02	70 ± 2	67 ± 16	0.5
Ca, wt.%	0.57 ± 0.04	0.582 ± 0.052	1.18 ± 0.08	1.08 ± 0.07	2.9 ± 0.1	2.70 ± 0.18	0.14 ± 0.02	0.1451(0.1229–0.1673)	0.03	–	–	–
Ce	0.84 ± 0.07	0.790 ± 0.076	1.22 ± 0.08	1.12 ± 0.10	–	–	–	0.81 (0.45–1.17)*	0.05	64 ± 2	64.5 ± 2.8	0.4
Cl	548 ± 47	573 ± 48	2662 ± 74	2840 ± 200	–	–	19520 ± 535	–	98	–	–	–
Co	0.38 ± 0.05	0.387 ± 0.042	0.20 ± 0.02	0.210 ± 0.025	–	0.10 ± 0.02	0.69 ± 0.04	0.68 (0.64–0.72)	0.01	13.3 ± 0.4	12.9 ± 1.2	0.15
Cr	1.4 ± 0.2	1.91 ± 0.22	1.3 ± 0.3	1.69 ± 0.13	0.90 ± 0.06	0.73 ± 0.22	4.7 ± 0.2	4.35 (3.98–4.72)	0.1	126 ± 3	136 ± 10	1
Cs	3.9 ± 0.3	3.61 ± 0.37	0.060 ± 0.005	0.076 ± 0.007	–	–	0.038 ± 0.003	–	0.025	6.4 ± 0.3	6.4 ± 0.44	0.1
Eu	0.048 ± 0.004	0.0499 ± 0.0094	0.0136 ± 0.004	0.0157 ± 0.0018	–	–	0.020 ± 0.001	0.021 (0.017–0.025)	0.0002	1.13 ± 0.03	1.18 ± 0.07	0.03
Fe	552 ± 32	(432)	534 ± 25	(460)	151 ± 15	146 ± 14	801 ± 15	607 (498–716)	10	39979±706	40800 ± 1900	100
Hf	–	–	0.23 ± 0.01	0.236 ± 0.020	–	–	0.20 ± 0.08	–	0.01	3.6 ± 0.2	3.66 ± 0.18	0.11
K, wt.%	1.66 ± 0.07	1.70 ± 0.12	1.86 ± 0.07	1.91 ± 0.12	1.33 ± 0.04	1.31 ± 0.12	1.09 ± 0.12	1.066 (1.008–1.125)	0.006	–	1.66 ± 0.032	–
La	0.98 ± 0.06	1.000 ± 0.070	0.58 ± 0.05	0.571 ± 0.046	–	–	0.30 ± 0.04	0.35 (0.30–0.41)	0.003	30.7 ± 0.5	33.7 ± 2.7	0.24
Lu	0.016 ± 0.002	0.0168 ± 0.0024	0.010 ± 0.002	0.0090 ± 0.0015	–	–	–	–	0.0007	0.35 ± 0.02	0.361 ± 0.039	0.07
Mn	0.16 ± 0.06	0.157 ± 0.011	0.192 ± 0.007	0.191 ± 0.012	–	3.52 ± 0.32	12.2 ± 0.7	–	0.44	–	316 ± 16	–
Na	26 ± 2	24.7 ± 3.2	382 ± 13	(350)	12466 ± 395	13100 ± 60	13190 ± 380	13016 (12530–13500)	13	12758±251	13500 ± 1500	190
Nd	–	–	–	–	–	–	–	–		28 ± 2	39.4 ± 3.1	2
Rb	89 ± 5	81.5 ± 6.5	11.7 ± 0.7	10.7 ± 0.7	2.9 ± 0.1	2.86 ± 0.40	5.1 ± 0.2	5.23 (5.1–5.4)	0.5	95 ± 3	99.9 ± 14.2	4.5
Sb	0.048 ± 0.002	(0.050)	0.048 ± 0.008	0.0655 ± 0.0091	0.027 ± 0.004	0.011 ± 0.002	0.015 ± 0.002	–	0.01	1.8 ± 0.1	1.96 ± 0.18	0.20
Se	0.075 ± 0.011	(0.076)			3.18 ± 0.08	2.83 ± 0.38	1.16 ± 0.03	1.07 (0.99–1.16)	0.04	–	0.78 ± 0.20	–
Sc	0.26 ± 0.02	0.266 ± 0.024	0.125 ± 0.005	0.123 ± 0.009	–	–	0.248 ± 0.005	0.25 (0.24–0.25)	0.001	14.5 ± 0.2	14.6 ± 1.1	0.01
Sm	0.158 ± 0.007	0.177 ± 0.022	0.101 ± 0.002	0.0944 ± 0.0082	–	–	0.091 ± 0.009	–	0.005	5.3 ± 0.4	5.61 ± 0.33	0.10
Ta	–	(0.008)	–	0.0186 ± 0.0023	–	–	–	–		1.00 ± 0.08	1.03 ± 0.09	0.08
Tb	0.026 ± 0.007	0.0265 ± 0.0024	0.013 ± 0.003	0.0135 ± 0.0011	–	–	–	–	0.0006	0.66 ± 0.10	0.696 ± 0.092	0.11
Th	0.038 ± 0.012	0.0343 ± 0.0048	0.15 ± 0.02	0.154 ± 0.013	–	–	0.100 ± 0.009	–	0.01	9.2 ± 0.2	9.78 ± 0.57	0.45
U	0.099 ± 0.015	–	0.078 ± 0.027	(0.049)	–	–	0.050 ± 0.004	–	0.004	2.4 ± 0.1	2.45 ± 0.24	0.30
V	1.6 ± 0.3	1.97 ± 0.37	0.86 ± 0.03	0.952 ± 0.163	–	–	2.87 ± 0.04	2.63 (1.95–3.31)		–	160 ± 11	–
Yb	0.13 ± 0.01	0.118 ± 0.013	0.052 ± 0.004	0.0527 ± 0.0066	–	–	–	–	0.0003	1.96 ± 0.03	2.24 ± 0.17	0.20
Zn	35.6 ± 0.9	34.7 ± 2.7	32 ± 2	33.5 ± 2.1	76 ± 1	67.1 ± 3.8	36.8 ± 0.6	35.35 (34.42–36.29)	0.3	103 ± 5	101 ± 8	2.8

Values in brackets are information values; uncertainties at 95% confidence interval for six replicate analysis.

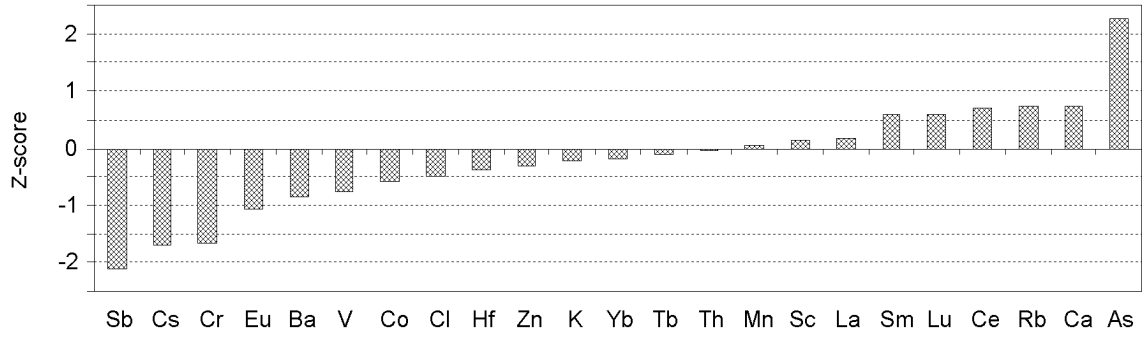

Fig. 1. Control chart (*Z*-score values) for elements in Mixed Polish Herbs (INCT-MPH-2)

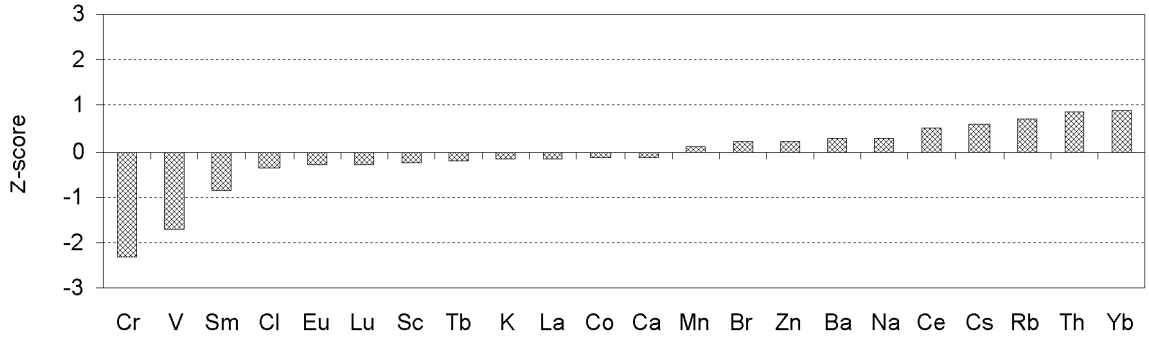

Fig. 2. Control chart (*Z*-score values) for elements in Tea Leaves (INCT-TL-1)

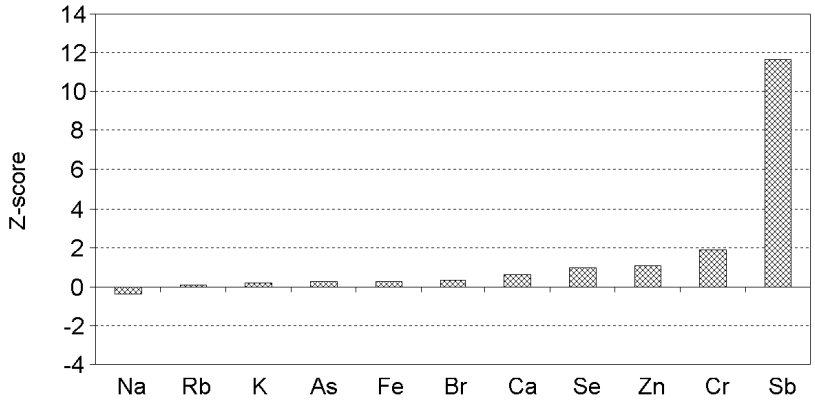

Fig. 3. Control chart (*Z*-score values) for elements in Fish Tissue (IAEA-407)

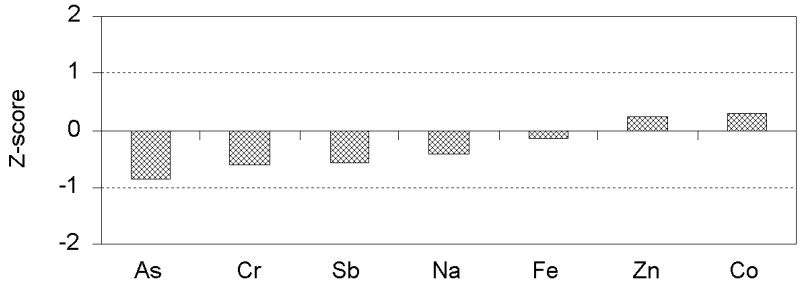

Fig. 4. Control chart (*Z*-score values) for elements in Marine Sediment (IAEA-433)

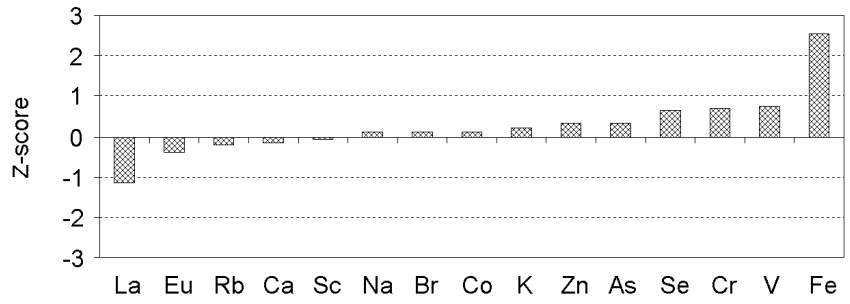

Fig. 5. Control chart (*Z*-score values) for elements in *Almeja – Venus Antiqua* (MR-CCHEN-002)

Conclusions

These results show the good performance of INAA methodology used at LAN-IPEN in analyzing biological and geological matrices with a very wide range concentration, providing results for up to 30 elements. The contribution of LAN in the certification of the reference materials analyzed was very important, as far as most of the results provided were used in the statistical evaluation of the certified value. INAA has proved to be an analytical technique adequate to characterize candidate reference materials.

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