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# Assessment of the Portuguese $k_0$-INAA laboratory performance by evaluating internal quality control data

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**Abstract** The Portuguese INAA laboratory processes approximately one thousand of multi-matrix samples per year, generating fifteen thousands of results in the same period, using the $k_0$ methodology. In order to ensure that the data produced meets the require quality any sample analysed is processed together with a reference material. Therefore, every year a large amount of results of many reference materials are generated. This work analysed a large database created with the results from the reference materials irradiated in the period 2009–2013. Zeta-scores were calculated and different control charts were created as function of the time period, irradiated mass, reference material and operator. The objective of this work was to recognise human errors, to identify deficiencies in the protocols and to improve the quality of the results generated by the laboratory.

**Keywords** $k_0$-Neutron activation analysis · Quality control · Reference materials · Zeta-scores

## Introduction

For nearly three decades, INAA using the $k_0$ standardization method is being applied in the Instituto Superior Técnico (formerly: Instituto Tecnológico e Nuclear) using the Portuguese Research Reactor (RPI), a 1 MW pool type reactor [1]. The irradiations are performed using regular in-pool devices or using fast moving pneumatic devices, essential for measurements with short-lived radionuclides. The laboratory has several facilities for counting of the induced activities, such as germanium detectors, automatic sample changers and a Compton suppression system [2]. The major research lines being pursued using $k_0$-INAA are related to the environment, epidemiology and nutritional fields.

The Portuguese Research Group has already shown the advantages of the technique in aerosol studies, such as the many elements that can be measured, the high degree of accuracy, whereas also little sample preparation is necessary [3–5]. Currently, the complete chemical characterization of the indoor [6–8] and outdoor [9–11] particles is used to elucidate the sources of the pollutants and the processes associated with their formation [12–15]. This will allow insight in local, regional and long-range transport [16–18] and, finally, to identify mitigation options focusing on the reduction of the air pollutant concentrations [19, 20]. The attractiveness of $k_0$-INAA for biomonitoring studies is reflected by (1) the large number of biomonitoring surveys performed by the group throughout international, national and regional levels [21], (2) its widespread use in the identification and characterization of emission sources [22] and (3) more recently, its application in the realm of human epidemiology [23].

The objective of the epidemiology research line is to establish unequivocal associations between pollution and morbidity and mortality. Respiratory problems, cardiovascular disease and carcinogenic incidence in the Portuguese population have been studied in association with chemical elements measured by $k_0$-INAA [24, 25].

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This research line also focuses on the assessment of occupational exposure to chemical elements and in the development of human bioindicators to be applicable for occupational exposure [26, 27].

In the nutrition field, different types of supplementation and their efficacy are studied [28, 29].

A wide variety of samples is processed in all these lines of research, typically in the order of 1,000/year at specific optimized analytical protocols depending on the matrix. Variables are (1) the mass of the samples; (2) the packaging procedure; (3) the irradiation position and (4) the irradiation, decay and counting times. The work process from the sample preparation until the spectrum analysis is performed by several students and scientists but obviously, results obtained by these different operators, under different protocols, using different detectors should be consistent with each other.

Therefore, the laboratory has to anticipate continuously on situations that can affect the quality of the results [30]. In order to ensure that the data produced meets the require quality, thus making it fit for the intended purpose, quality assurance and quality control has to be implemented. Control charts are a valuable tool in this for monitoring some of the variables [30, 31]. The analysis of reference materials and the resulting patterns in control charts is therefore the onset to establish if systematic errors may have been made, and the associated need for actions aiming the improvement of the performance [32].

The objective of the work described in this paper was to recognise human errors, to identify deficiencies in the protocols and to evaluate the quality of the analysis results of different reference materials.

## Experimental

For internal quality control, in the Portuguese $k_0$-INAA laboratory any sample analysed is processed together with a reference material, which is chosen according to (1) the known amount of the elements of interest; (2) the suitability for irradiation and measurement of the material and (3) the detectability of the radionuclides of the elements of interest under these conditions. Table 1 presents an overview of the variety and frequency of the principal reference materials used in the period 2009–2013.

The reference materials were co-irradiated with the samples in two different positions near the reactor-core depending on the matrix of the samples. The certified reference material NIST SRM-1633a (Coal Fly Ash), was irradiated with aerosol filters in Cell 55, which has a thermal neutron flux of about $7.0 \times 10^{12}$ cm$^{-2}$ s$^{-1}$ ($f = 50$ and $\alpha = 0.005$). The other reference materials were irradiated with soils, plants, lichens and cereals in Cell 56,

**Table 1** Irradiation and measuring conditions for the reference materials analysed in the period 2009–2013

| Reference material | | | No. of analysed RM | Associated samples | Irradiated mass (mg) | Irradiation conditions | | | | Measuring conditions | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Thermal flux (cm$^{-2}$ s$^{-1}$) | $f$ | $\alpha$ | Irr. T (h) | Wait T (days) | Meas T (h) | Wait T (days) | Meas T (h) |
| NIST-1633a | [33] | Coal Fly Ash | 119 | Aerosols | 11–181 | $7.0 \times 10^{12}$ | 50 | 0.005 | 5 | 3–4 | 7 | 28 | 7 |
| IAEA-336 | [34] | Lichens | 36 | Lichens | 134–474 | $3.9 \times 10^{12}$ | 69 | 0.0045 | 5 | 3–4 | 2 | 28 | 2 |
| IAEA-Soil7 | [35] | Soil | 12 | Soils | 139–207 | $3.9 \times 10^{12}$ | 69 | 0.0045 | 1 | 3–4 | 1.5 | 28 | 2.5 |
| IGGE-GBW07406 | [36] | Soil | 11 | Soils | 65–151 | $3.9 \times 10^{12}$ | 69 | 0.0045 | 1 | 3–4 | 1.5 | 28 | 2.5 |
| IGGE-GBW07404 | [36] | Soil | 5 | Soils | 65–111 | $3.9 \times 10^{12}$ | 69 | 0.0045 | 1 | 3–4 | 1.5 | 28 | 2.5 |
| NIST-1568a | [37] | Rice flour | 14 | Cereals | 49–246 | $3.9 \times 10^{12}$ | 69 | 0.0045 | 5 | 3–4 | 4 | 28 | 4 |
| NIST-1567a | [38] | Wheat flour | 3 | Cereals | 77–126 | $3.9 \times 10^{12}$ | 69 | 0.0045 | 5 | 3–4 | 4 | 28 | 4 |
| NIST-1572 | [39] | Citrus leaves | 10 | Plants | 135–143 | $3.9 \times 10^{12}$ | 69 | 0.0045 | 5 | 3–4 | 3 | 28 | 3 |
| INCT-OBTL5 | [40] | Oriental tobacco leaves | 4 | Plants | 149–152 | $3.9 \times 10^{12}$ | 69 | 0.0045 | 5 | 3–4 | 3 | 28 | 3 |

*Irr. T* irradiation time, *Wait T* waiting time, *Meas T* measuring time, *NIST* National Institute of Standards and Technology, *IAEA* International Atomic Energy Agency, *IGGE* Institute of Geophysical and Geochemical Exploration, *INCT* Institute of Nuclear Chemistry and Technology

which has a thermal neutron flux of about $3.9 \times 10^{12}$ cm$^{-2}$ s$^{-1}$ ($f = 69$ and $\alpha = 0.005$). Irradiation times are also presented in Table 1.

The induced activity of the samples and the reference materials was measured with two calibrated Ge detectors, each with a FWHM approximately 1.85 keV at 1,332.5 keV and a relative efficiency of 30 %. Measuring conditions are presented in Table 1. The gamma-ray spectra were interpreted by $k_0$-IAEA program.

A large database was created with the results for nine quality control reference materials, obtained by six operators and under different analytical protocols, and Zeta scores were calculated following the Eq. 1:

$$\zeta = \frac{x_{lab} - x_{ref}}{\sqrt{u_{lab}^2 + u_{ref}^2}} \quad (1)$$

in which $x_{lab}$ is the mass fraction of the measured result of the element in the reference material, $x_{ref}$ is the certified/indicative mass fraction, $u_{lab}$ is the combined standard uncertainty of the measured result and $u_{ref}$ is the combined standard uncertainty of the certified value. The combined standard uncertainties are derived from the listed expanded uncertainties, ignoring, if applicable, the uncertainty from the bias since this value is not given by the supplier. For non-certified values, which are not furnished with their uncertainties, the expanded uncertainties were set to as 10 % relative of the values given in certificate [41]. The results were interpreted according the following classes: $|\zeta| \leq 2$, considered as a satisfactory level; $2 < |\zeta| < 3$, classified as a questionable level and $|\zeta| \geq 3$, which is an unsatisfactory level [42].

## Results

Figure 1, which presents the percentage of measurements classified by Zeta-score level, indicates that 73 % of the values are at a satisfactory level, 9.7 % are at a questionable level and 17 % are at an unsatisfactory level. Results also show that 67 % of the Zeta-scores present a negative value indicating the existence of a systematic bias. This could be a systematic error due to the measurement and/or preparation of the flux monitor since this affects all elements in the same way.

The percentage of values in the interval $-3 < \zeta < 3$ was calculated for each element. Mo, Se, U and Zn presented percentages higher than 90 %; Ba, Br, Ca, Cs, Rb, Sb, As, Ce, Co and Sm had percentages between 80 and 90 % and K, La, Na and Sc were within the interval 75–80 %. Cr and Fe presented the lowest percentage of values in the interval $-3 < \zeta < 3$ (66 and 68 %, respectively).

In order to identify the sources of non-conformance ($|\zeta| \geq 3$) data from the reference materials were displayed

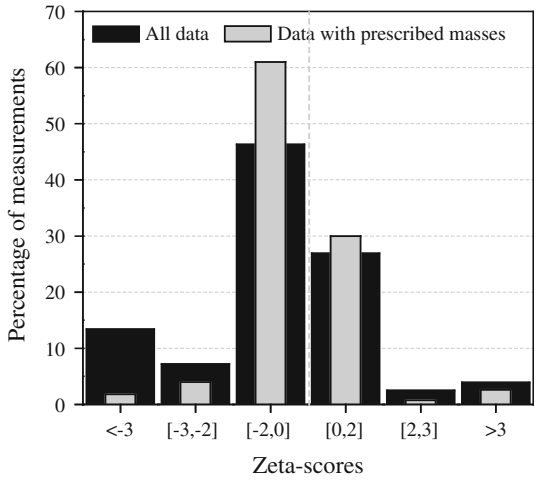


**Fig. 1** Percentage of measurements classified by Zeta-scores class ($|\zeta| \leq 2$, satisfactory level; $2 < |\zeta| < 3$, questionable level and $|\zeta| \geq 3$, unsatisfactory level) for all data and only for data associated with masses higher than the prescribed by the reference material supplier

in various control charts where Zeta-score was displayed as a function of (1) the analysis date; (2) the mass of the element; (3) the reference material and (4) the operator. These charts were made in order to check the results from a single analysis (such as in graphs analysing the Zeta-score in function of the analysis data and of the mass of the elements) or from a group of analysis (in case of the graphs where Zeta-score was plotted in function of the reference material and of the operator).

Figure 2 shows the Zeta-score as a function of the date of the analysis discriminated by reference material. This control chart was created in order to indicate incidental deviations and trends. Results showed that in the year 2012, the performance of the laboratory decreased, especially for the certified reference material NIST SRM 1633a (Coal Fly Ash), which presented $|\zeta| \geq 3$ for the elements As, Br, Ce, Co, Cs, Fe, La, Sb, Rb, Sb, Cr, Sm, U and Zn.

Figure 3 presents the Zeta-score as a function of the mass of the element that can indicate problems associated with detection limits and inhomogeneity of the sample. Information can be obtained on the performance of the technique for the determination of an element at a certain level in a given matrix. Results from this control chart show that, for the elements identified previously and for the Coal Fly Ash, $|\zeta| \geq 3$ were associated with samples which had the lowest element masses. Table 1 shows that the irradiated masses of this certified reference material varied between 11 and 181 mg, which is an amount lower than the minimum required by the producer. The use of small amounts of masses was done in order to allow the co-irradiation of this reference material with aerosol filters without becoming excessively activated. However, the irradiation of small amounts of material can pose problems,

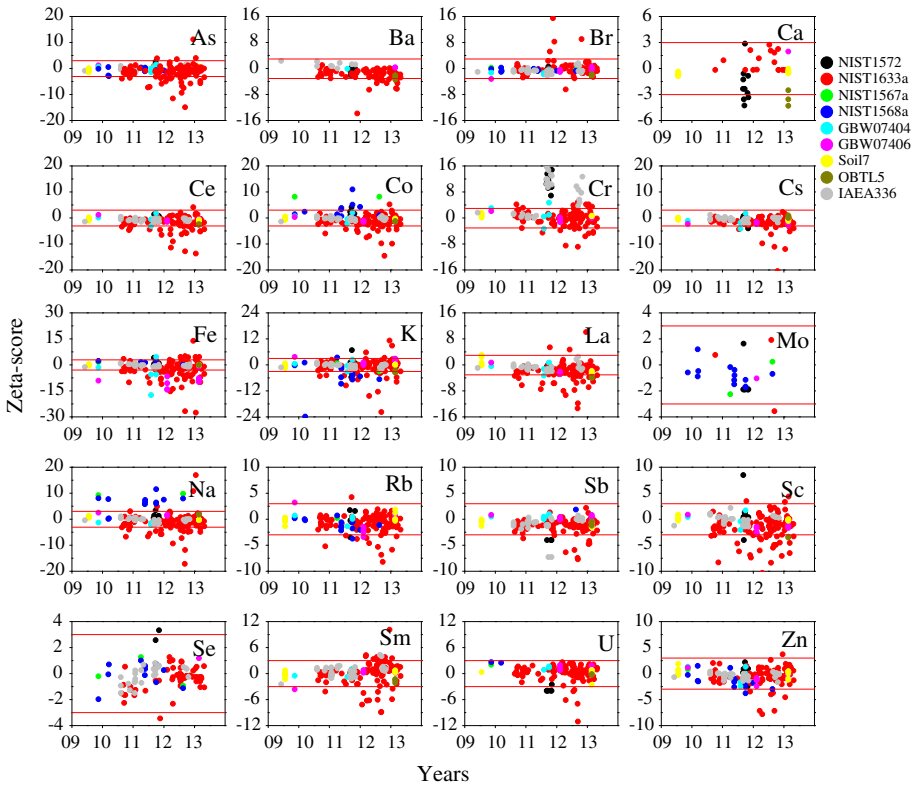


**Fig. 2** Control chart showing the Zeta-score as a function of the analysis date (grossly indicated by the years in this millennium) discriminated by reference material and element

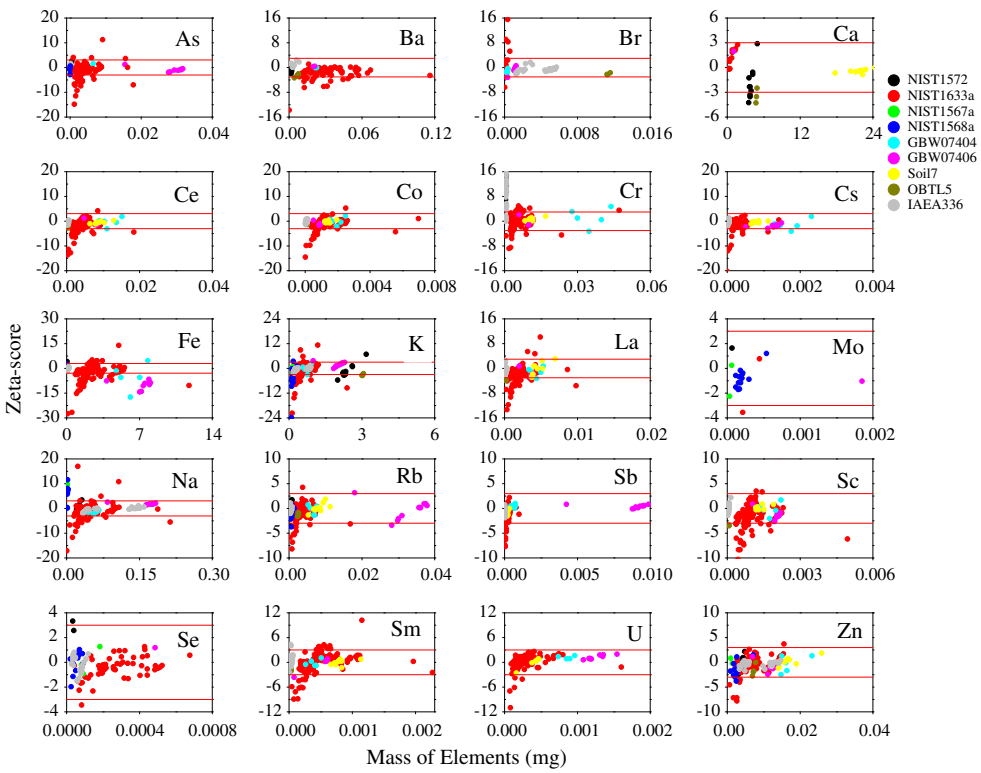


**Fig. 3** Control chart showing the Zeta-score as a function of the mass of the elements discriminated by reference material and element

due to the homogeneity of the sample or due to the proximity of the detection limits, and this was reflected in the control chart presented in Fig. 3. Therefore, it is probable that the analytical result for the real samples co-irradiated with the reference material, in this case the aerosol filters, are correct but not revealed due to the low amount of

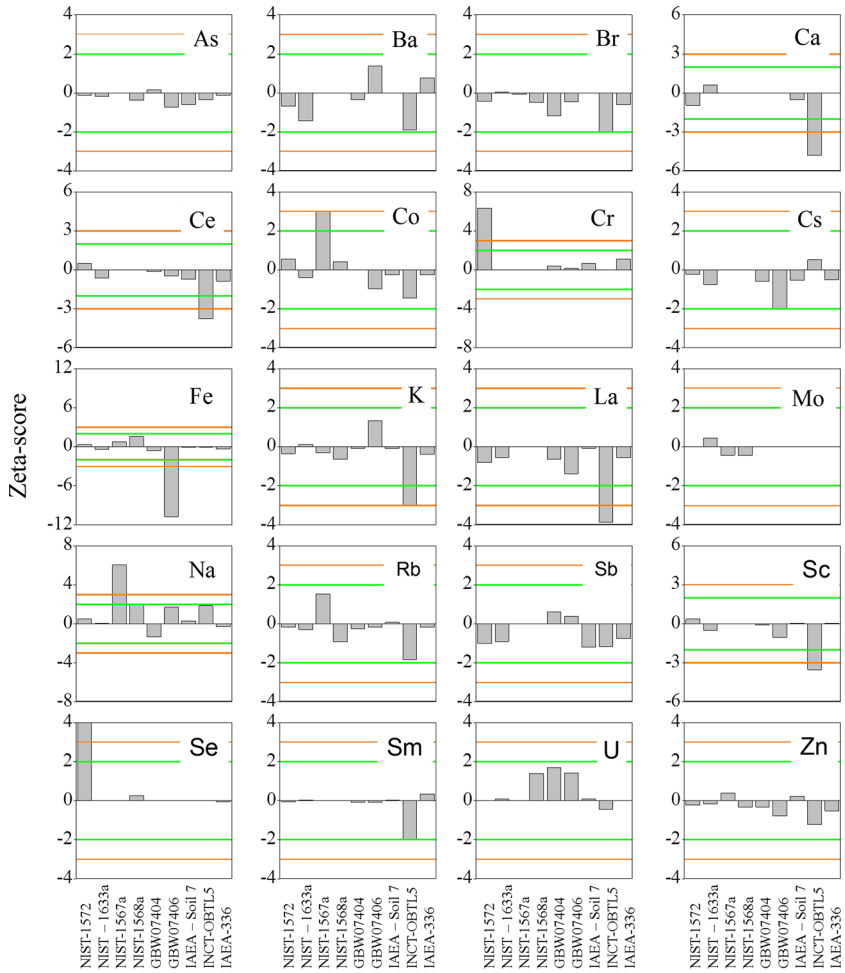


**Fig. 4** Control chart showing the Zeta-score as a function of the reference material discriminated by element

reference material that it was used. This fact reflects a problem that exist on the quality control of the aerosol filters analysis, which is the lack of adequate reference materials (with a similar matrix) to be co-irradiated with these samples. The few reference materials that exist in the market cannot be irradiated with all batches of filters due to economic reasons. In order to overpass this restriction, the Portuguese $k_0$-INAA laboratory applies three methodologies in order to control the quality of aerosol filters analysis: (1) the preparation of simulated air-filters by spiking known amounts of standard solutions onto Nuclepore polycarbonate filters [43]; (2) the analysis of different parts of aerosol filters by $k_0$-INAA [44] and (3) the parallel analysis of different parts of the same filter by $k_0$-INAA and PIXE [44].

The highest Zeta-values for Cr were observed for IAEA336 and NIST SRM 1572, which are the materials that presented the lowest mass fraction for this element (1.06 and 0.8 mg $kg^{-1}$, respectively). Table 1 indicates that the irradiated masses of IAEA336 varied between 134 and 474 mg and results showed that for masses varying between 135 and 207 mg the Zeta-value was 10 whereas for masses varying between 392 and 474 mg the Zeta-value was 0.5. Therefore, also for this element the low sample masses are the probable origin of $|\zeta| \geq 3$.

Since the control charts present in Fig. 3 indicated that the higher $|\zeta|$ were obtained when operators used masses lower than the indicated by the reference materials providers, the percentage of measurements classified by Zeta-score level was re-calculated only considering the references materials that were analysed with masses higher than the prescribed (Fig. 1). Results indicated that results improved significantly being 91 % of the values at a satisfactory level, 4.7 % at a questionable level and 4.3 % at an unsatisfactory level.

Figure 3 shows that for Fe high Zeta-scores were obtained for the reference material GBW07406 which has a Fe indicative value of 61,015 mg $kg^{-1}$. Results showed a very good precision (average = 52,191 mg $kg^{-1}$ and standard deviation = 3,360 mg $kg^{-1}$) and counting statistical errors lower than 2 %. Therefore, differences between measured and reference values seem to be related with the quality of the indicative value.

Figure 4 presents a control chart with the Zeta-score given as a function of the reference material discriminated by element. In this case it was considered $x_{lab}$ as the

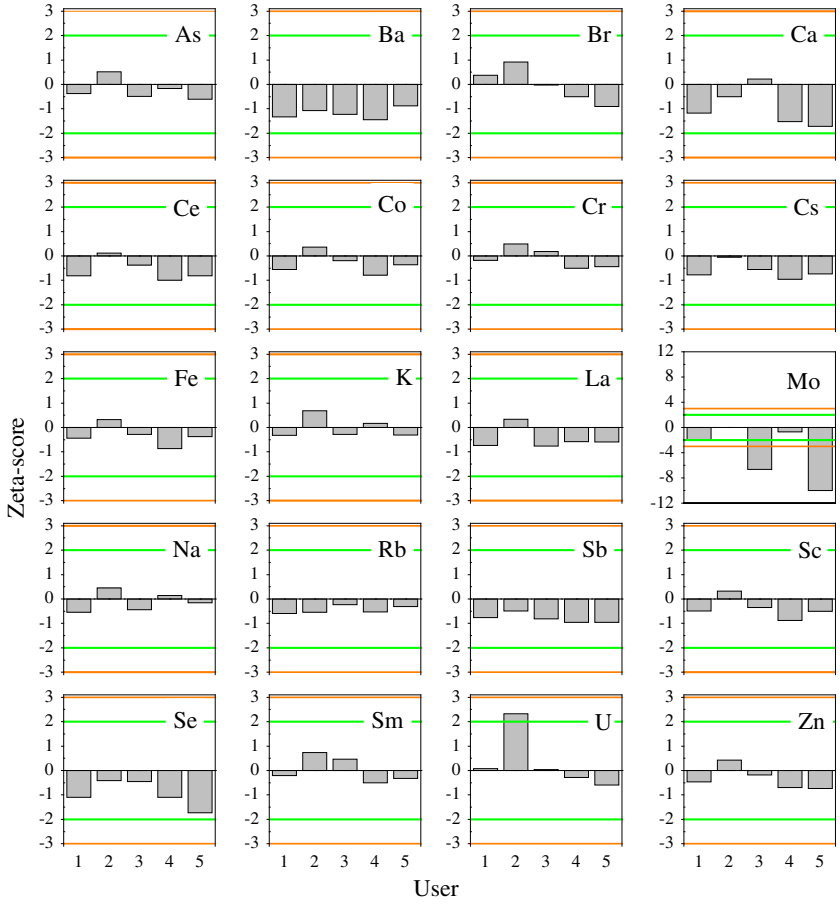


**Fig. 5** Control chart showing the Zeta-score as a function of the user discriminated by element for the certified reference material NIST SRM 1633a

average of the mass fraction obtained for each reference material and $u_{lab}$ the respective standard deviation. With this type of chart, a systematic bias for all elements in one specific reference material may indicate an erroneous way of e.g., moisture content correction, drying or storage. Results showed that the results obtained for the reference material OBTL5 (oriental tobacco leaves) are the worst: Ca, Ce, La and Sc at the unsatisfactory level and Ba, Br, K and Sm at a questionable level.

A control chart displaying the Zeta-score as a function of the user was made for NIST SRM 1633a, which was the most frequently used reference material, aiming the identification of analyst depending results. Figure 5 showed that in general there isn't any analyst dependency.

## Conclusions

In the Portuguese $k_0$-INAA laboratory, all users analyse their samples together with a reference material to assess if no systematic errors have been made. The results of these analyses can be used in more advantageous way when they are all put together in a database, and control charts are created to sort and correlate data.

In the present work the assessment of control charts identified sources of errors. The mass of the irradiated samples was identified as the main cause for weaker results for the reference material irradiated in 2012, due to the increase of inhomogeneity of measurands in smaller analysed masses. It is therefore essential to use the reference materials according the producers' specifications and to select them according the intended purpose.

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