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# Uncertainty of lead in foods with internal control data: ISO 21748 approach and Monte Carlo.

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## Abstract

One of the simplest approaches for estimating uncertainty in trials, is the one used in the ISO 21748:2010 standard, where repeatability, reproducibility and trueness data are used for its calculation. This paper compares a systematic approach to this, based on the use of internal control data in terms of recovery tests, compared to those obtained by the Monte Carlo probabilistic method. Both methods were applied to the routine laboratory samples for two years for the analysis of lead in foods by Inductively coupled plasma atomic emission spectrometry (AES-ICP).

## Materials and methods

### 1. Estimating uncertainty

The Monte Carlo method (MCM) is a probabilistic method and complementary to the GUM method as published by ISO in 2008. In this systematic, uncertainty is obtained by the probability distributions of the "inputs" for numerical approximations of the probability distributions of the values obtained by the model (Figure 1 y 2).

An alternative to the previous estimation of uncertainty is the use of the repeatability and reproducibility values based on the concepts of repeatability and reproducibility of ISO 21748. As an approximation to the indicated in the above mentioned Norm, the repeatability (start and end of the sequence) and reproducibility (different days) data of the internal control were used, expressed as recovery (Figure 1). The data were filtered to those in which the bias obtained in terms of recovery were not significant.

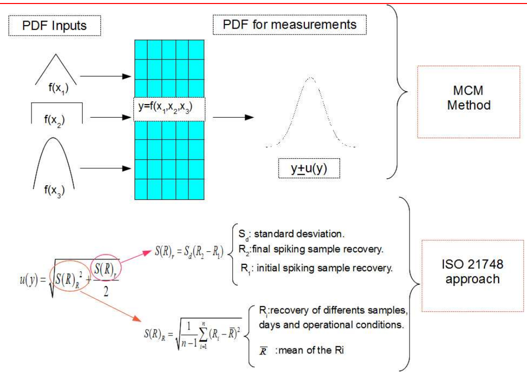



Fig. 1. Methodologies used in the calculation of uncertainty

### 2. LEAD IN FOODS (AES-ICP)

The analysis of lead in food was conducted by an internal procedure validated and accredited by ENAC using AES-ICP (Jobin Yvon mark, Ultima model) after sample calcination at 550 ºC, redissolving ashes with 6M HCl and making up with ultrapure water. The concentration of acid in the standards was similar to that of the samples. The systematic quality assurance procedure, from which data were collected for estimation of uncertainty, involved spiking different matrices with a known amount of a lead standard, as shown with three examples in Table 1.

| Commodity | Conc obtained (mg·kg⁻¹) | Final vol. (ml) | Weight (g) | Theoretical conc. (mg·kg⁻¹) |
|---|---|---|---|---|
| Rice | 0,19 $\pm$ $s_d$ | 10 $\pm$ 0,025 | 5 $\pm$ 0,2 | 0,24$\pm$ $s_d$ |
| Sugar | 0,19 $\pm$ $s_d$ | 10 $\pm$ 0,025 | 5 $\pm$ 0,2 | 0,21$\pm$ $s_d$ |
| Milk | 0,20 $\pm$ $s_d$ | 10 $\pm$ 0,025 | 5 $\pm$ 0,2 | 0,19$\pm$ $s_d$ |

Table. 1. Exemples of results of quality assurance.

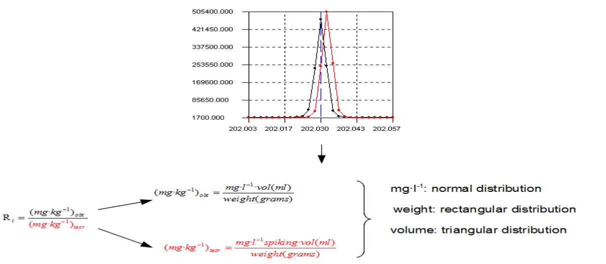
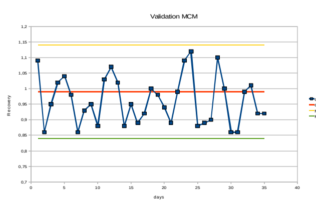



Fig. 2. Mathematical model used in testing lead in foods.

## Results

| Calculation | Average of Recovery (y) | Uncertainty u(y) |
|---|---|---|
| ISO 21748 | 0,95 ( M=25) | 0,18 |
| MCM | 0.99 (M=$10^5$) | 0,15 |



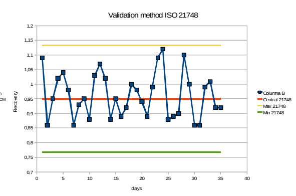




Table. 2. Results obtained by application of MCM and ISO 21748 approach.
Figure 3 y 4. Validation of the results obtained the following year.

The approaches used to estimate the uncertainty of the Monte Carlo method using spreadsheets were; for the normal probability distribution $N(\mu;\sigma^2)$ "NORM.INV", in the case of a rectangular probability distribution, by approximation a+(b-a)*RAND() were "a" is the lowest end of the range and "b" the superior. Finally, for the triangular probability distribution (final volume) a VBA macro was made.

On the other hand the values of $S(R)_r$ y $S(R)_R$ were obtained immediately by using the subtotals in the spreadheet, resulting in the estimation of uncertainty in Table 2 (ISO 21748 appr.).

The speed of calculation for Monte Carlo simulation, with different computers was, 2 minutes for a PC with 2,5 GHZ and 4GB RAM and approximately 8 minutes for a laptop with 1,73 GHz and RAM 3062MB.

The results obtained by the laboratory during the first year were used in the estimation of uncertainty, and over the next year to check which were the best suited to a method and another.

## Discussion

The results obtained by both methods (Table 2) show similar values, although slightly lower for the Monte Carlo method (uncertainty 0.15 versus 0.18). However, the Monte Carlo method reflects, more accurately, both the central tendency as the internal control uncertainty. This is seen when representing the experimental results of the internal control for a year, in a simple graphical control of the central value and the extreme values obtained from the calculation of uncertainty using both methods.
The Monte Carlo method can be a simple way to estimate the uncertainty using spreadsheets, presenting no more difficult than the iteration sufficient to achieve the desired probability level. Using spreadsheets, the probability distribution of the a triangular type has more difficulty although the VBA programming is available via mail from the authors.

## References

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