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EVALUATION OF MEASUREMENT UNCERTAINTY OF METALS IN SOILS

Margarida Maria Correia dos Santos[1], Sheila Alves[1], Maria Ascensão Trancoso[2]

[1]Instituto Superior Técnico, Lisboa, Portugal, mcsantos@ist.utl.pt
[2]Instituto Nacional de Engenharia, Tecnologia e Inovação, Lisboa, Portugal,

Abstract: Estimation of measurement uncertainty of the metal content in different soils was done using validation and quality control data. Precision under within-laboratory reproducibility conditions was estimated from duplicate analysis. Trueness was determined as recovery of the analyte from two certified reference materials (CRM). The CRM properties on the results obtained is critically evaluated.

Keywords: Uncertainty, CRM, soil.

1. INTRODUCTION

It is now fully recognized that an essential part of any quantitative analysis is the evaluation of uncertainty associated with the result being estimation of uncertainty of a measurement a standard requirement of the ISO/IEC 17025:2005 [1]. Whatever uncertainty estimation approach is used the main stages are: specification of the measurand, identification of sources of uncertainty, quantification of uncertainty components and combination of individual uncertainty components.

As known, the major sources of variability can often be assessed by method validation through quality control actions. In these conditions, the quantification of uncertainty contributions can be done using pre-existing quality control and validation data [2]. In this work, this approach is used to calculate the measurement uncertainty associated with the metal content of soils from serpentine and non-serpentine areas from the north-east of Portugal. Commonly they have high levels of trace metals like Ni, Cr and Co and low Ca/Mg ratios. Two different CRM were used and the results obtained for the measurement uncertainty are critically evaluated on the basis of the approach used in the calculations and the quality of the CRM.

2. METHODS

Soil samples collected at 0–15 cm depth from the surface in NE Portugal, were air-dried, crushed with an agate mortar and pestle and then stored in plastic containers. An acid mixture (HNO_3+HF+$HClO_4$) was used to solubilise Al, Ca, Fe, K, Mg, Na, Mn, Cr, Cu, Ni, and Zn [3]. All elements were determined by Flame Atomic Absorption Spectrometry (FAAS). The CRM used were: soil sample SO-2 from the Canada Centre for Mineral and Energy Technology and river clay sediment LGC 6139 from the Laboratory of the Government Chemist.

3. RESULTS AND DISCUSSION

The metal content of eight soil samples was determined following a quality assurance program previously established. In order to provide reliable data, quality control actions were also implemented [3].

The measurand, the mass concentration of total metal, C_M in soils (mg kg^{-1}) expressed in dry basis is given by eq. 1:

$$C_M = \left[C_x \times \frac{V}{m} \times F_{dil} \times \frac{1}{1-w_{105}} \right] \times f_{trueness} \times f_{precision} \qquad (1)$$

where C_x is the interpolated analyte concentration (mg l^{-1}), V the volume of the attack solution (ml), m the amount of sample taken for analysis (g), F_{dil} the dilution factor and w_{105} the moisture content of the sample determined by drying an independent aliquot of the sample at 105±5ºC. Figure 1 shows the cause – effect diagram for C_M. The main branches identify the influence quantities (C_x, V, m, F_{dil} and w_{105}). A branch for precision was added, that combines all the individual repeatability contributions as well as a second branch for the trueness (recovery).

In this work an intralaboratory approach for uncertainty evaluation based on method validation studies and quality control data was used.

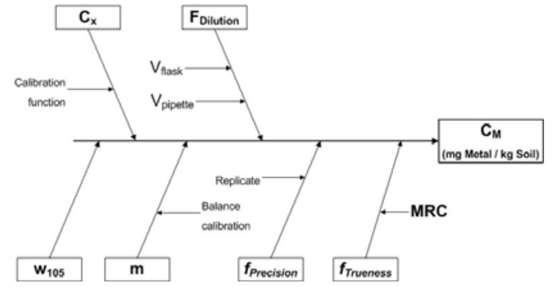

Figure 1 – Cause - effect diagram for the concentration of total metal in soils, expressed in dry basis.

So, the combined standard uncertainty for C_M, $u_c^{rel}(y)$, was determined by the contribution of two main components, eq. 2, which assumes precision, expressed as relative standard deviation *(RSD)*, approximately constant within the working range and the relative uncertainty of the recovery, $u^{rel}(\overline{R}_m)$, independent of the concentration of the analyte [2].

$$u_c^{rel}(y) = \sqrt{RSD^2 + \left[u^{rel}\left(\overline{R}_m\right)\right]^2} \qquad (2)$$

In each working range RSD was calculated by use of eq. 3:

$$RSD\ (\%) = \frac{s}{\bar{x}} * 100 \tag{3}$$

where $\bar{x}$ is the average concentration and s, the standard deviation, is given by eq. 4:

$$s = \frac{\bar{R}}{d_2} \tag{4}$$

with $\bar{R}$ the mean value of each range and d a tabulated factor for duplicate sets [2]. RSD values lower than 6% were obtained, indicating a good precision of the analytical procedure.

Trueness was estimated in terms of overall recovery obtained from the analysis of independent sets of CRMs. The $u^{rel}(\bar{R}_m)$ values were calculated using eq. 5:

$$u^{rel}(\bar{R}_m) = \frac{u(\bar{R}_m)}{\bar{R}_m} = \sqrt{\left(\frac{s_{obs}^2}{n * C_{obs}^2}\right) + \left(\frac{u_{CRM}}{C_{CRM}}\right)^2} \tag{5}$$

where $\bar{R}_m$ is the mean recovery given by eq. 6,

$$\bar{R}_m = \frac{\bar{C}_{obs}}{C_{CRM}} \tag{6}$$

C_{obs} and C_{CRM} are the experimental and listed concentrations of a metal in the CRM, respectively, s_{obs} is the standard deviation from replicate analysis of the CRM, $u(C_{CRM})$ is the standard uncertainty of the certified value for the CRM and n is the number of replicates.

Two CRM were used. Since the samples analysed for metal content were different soils, the CRM reference soil sample SO-2 was in principal more suitable from the point of view of matrix-matched. However, river clay sediment LGC 6139 was also used due to the low Nickel concentration in SO2. In figure 2 the relative uncertainty estimated using LGC 6139 (black) and SO-2 (grey) CRMs are shown for each metal. As can be seen significant differences can be found in the values depending on the CRM. A major factor controlling the value of the relative uncertainty of the recovery is the standard uncertainty of the certified value $u(C_{CRM})$. With the exception of Ni, relative uncertainty associated with SO-2 were further used to calculate $u^{rel}(\bar{R}_m)$.

Finally, the expanded uncertainty $U(y)$ was calculated by eq. 7:

$$U(y) = k \times u_c(y) \tag{7}$$

using a coverage factor of k = 2, which gives a level of confidence of approximately 95%.

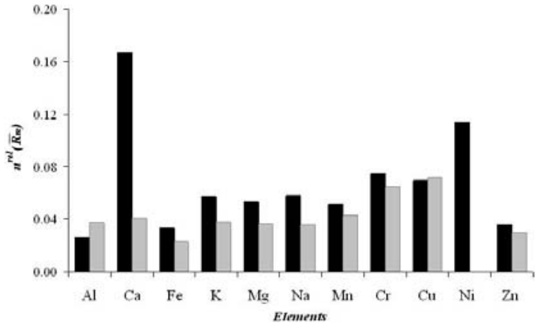

Figure 2. Relative uncertainty ($u^{rel}(\bar{R}_m)$) estimated using LGC 6139 (black) and SO-2 (grey) CRM.

In table 1 are shown the results for the metals composition of the soils with the corresponding expanded uncertainty. Higher Ni concentrations and lower Ca/Mg ratio were obtained for samples 1-6 corresponding to serpentine soils.

4. CONCLUSIONS

Estimation of uncertainty is neither a routine task nor a purely mathematical one. It depends on detailed knowledge of the nature of the measurand and of the measurement. However, this work shows that much of the data required to produce estimate of measurement uncertainty can be provided by studies routinely undertaken for validation purposes namely precision and trueness studies. The user should now how to look for the most appropriate CRM. Aspects like suitable matrix-matched and analyte concentration level should be taken into account, but it is also important the quality of the CRM.

ACKNOWLEDGMENTS

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Table 1. Chemical characterization of the soils. All results are expressed on a dry sample weight basis.

Soils	Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	Na (%)	Mn (%)	Ni/10^2 (mg kg^{-1})	Cr/ 10^3 (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})
1	4.0±0.5	1.5±0.3	10±1	0.39±0.06	5.8±0.8	0.42±0.08	0.24±0.04	28±7	29±5	29±5	73±8
2	4.1±0.6	1.5±0.3	10±2	0.39±0.06	5.9±0.9	0.43±0.08	0.25±0.04	28±7	29±5	29±5	92±10
3	4.0±0.5	1.8±0.3	11±2	0.33±0.05	6±1	0.39±0.07	0.23±0.04	33±8	31±5	31±5	87±10
4	4.4±0.6	1.7±0.3	12±2	0.34±0.05	7±1	0.42±0.08	0.24±0.04	34±8	33±6	33±6	79±9
5	4.1±0.6	1.4±0.3	12±2	0.27±0.04	7±1	0.29±0.05	0.27±0.04	38±10	33±6	33±6	120±13
6	4.8±0.6	1.6±0.3	11±2	0.51±0.08	5.9±0.9	0.49±0.09	0.27±0.04	29±7	30±5	30±5	98±11
7	8±1	7±1	7±1	0.09±0.01	2.9±0.4	1.7±0.3	0.14±0.02	0.8±0.2	39±6	39±6	55±6
8	9±1	6±1	7±1	0.10±0.02	2.4±0.4	1.6±0.3	0.12±0.02	0.6±0.2	31±5	31±5	53±6