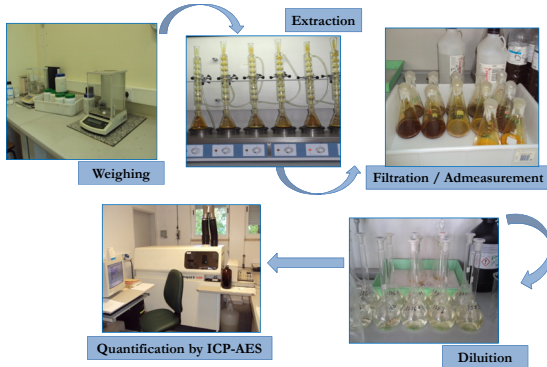


Objective

To develop a strategy for the internal quality control of the determination of aqua regia extractable elements, Zn, Pb, Cu, Cr, Cd and Ni, in organic soil improvers and urban sewage sludges following EN 13650:2001 and ISO 22036:2008 standards.

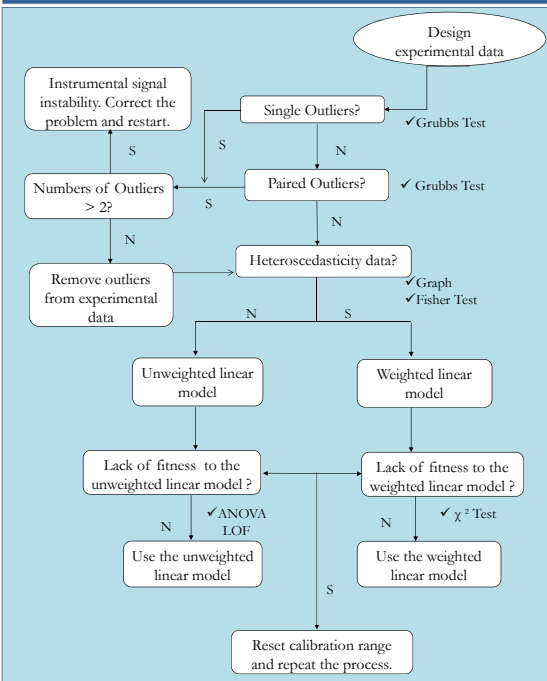
Measurement Procedure



Measurement Procedure Validation

- ✓ Validation of the linear regression model used for the calibration
 - ✓ Limit of quantification
 - ✓ Intermediate precision
 - ✓ Trueness
- ✓ Evaluation of the measurement uncertainty

Validation of the Instrumental Calibration Procedure



Internal Quality Control

In routine analysis, the measurement performance is assessed using the following tools and criteria:

- Calibration curve check:
Criterion: i) $r \geq 0.999$ and ii) Analysis of STD (see below);

- Analysis of standard solutions (STD) of heavy metal for controlling ICP-AES performance:

Criterion: metrological compatibility of estimated (a) and known (b) concentration of STD (uncertainty components to be considered: s_{inter} and u_{std}):

$$1.1 \quad |a - b| \leq k \sqrt{(u_a)^2 + (u_b)^2}$$

- Analysis of blank samples:

Criterion: Signal smaller or equal to the one estimated for the limit of detection [$3/10 \cdot LoQ \cdot b_{bl}$];

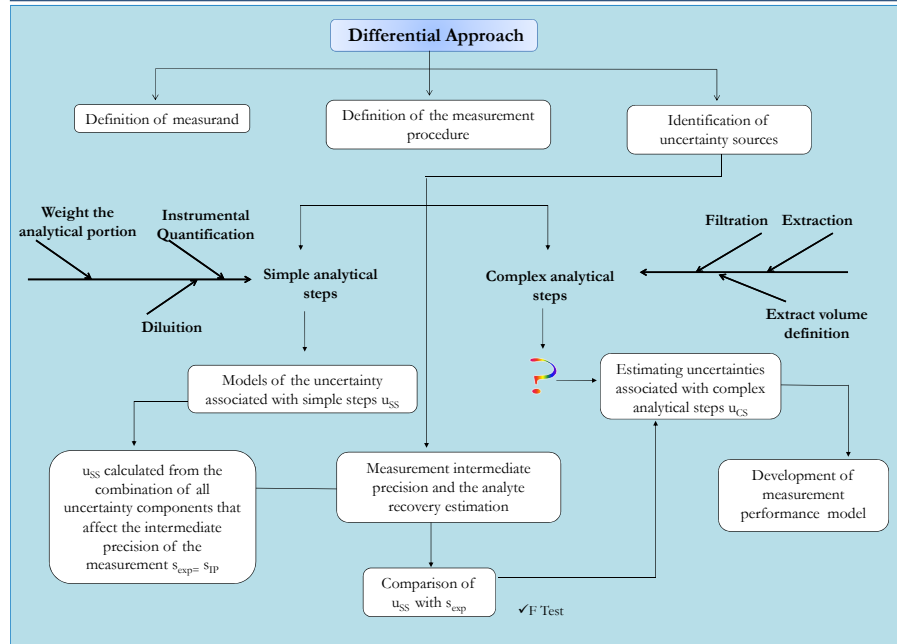
- Duplicate measurements performed in repeatability conditions:

Criterion: $1.2 \quad |A1 - A2| \leq 2.8 s_r$

- Analysis of a Reference Material of soil improvers and sludges (MR) (different from the used at the validation):

Criterion: metrological compatibility of estimated (A) and known (B) concentration of MR (uncertainty components to be considered: All): $1.3 \quad |A - B| \leq k \sqrt{(u_A)^2 + (u_B)^2}$

Evaluation of the Measurement Uncertainty



Results

Limit of Quantification (LoQ)

The limit of quantification was estimated through the analysis of blanks in intermediate precision conditions and by using regression model parameters from a calibration curve built from signals collected in different days. Equation 1.4 and 1.5 respectively.

$$1.4 \quad LoQ = 10 \times S_b$$

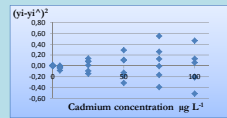
$$1.5 \quad LoQ = (10 \times S_{(y/w)}) / b_w$$

Heavy metals	LoQ $\mu\text{g L}^{-1}$	
	Blanks	Calibration
Copper	110	20
Zinc	485	78
Lead	19,7	20
Chromium	1,59	0,45
Cadmium	14,2	15
Nickel	157,4	116

wherein S_b is the blanks standard deviation, expressed in concentration units, the $S_{(y/w)}$ is weighted residual standard deviation, and b_w the slope estimated by weighted linear regression model.

Validation of the linear weighted regression model for the calibration

The evaluation the homoscedasticity of the variance of the instrumental signal and the fitness of the regression model to describe the calibration curve was based on experimental data with the following design: 6 concentrations levels and 6 replicates at each level. The 36 signals were collected in intermediate precision conditions.



1.1. Residual plot of cadmium

All elements, revealed heteroscedastic variances (like the figure 1.1) and produced calibration curves adjusted to the weighted linear regression model.

Measurement Uncertainties

Table 1.3 presents the relative standard uncertainty (u_{CS}) associated with the combined effect of all complex analytical steps. The overall measurement uncertainty is estimated by the equation 1.8.

$$1.8 \quad u_x = \sqrt{(u_m)^2 + (s_{inter})^2 + (u_{RM})^2 + (u_{std})^2 + (u_{CS})^2 + (u_E)^2}$$

Wherein u_m , s_{inter} , u_{RM} , u_{std} , u_{CS} , and u_E represents the relative standard uncertainty associated with the weighing, sample signal interpolation, analyte recovery, calibration standard preparations, the complex analytical steps and dilution factor respectively.

Intermediate Precision

For the determination of measurement intermediate precision, 6 samples of reference materials were analysed in 3 weeks, equation 1.6

$$1.6 \quad s'_{ip} = \sqrt{\frac{\sum_{i=1}^n \sum_{j=1}^t (\bar{x}_{ij} - \bar{x}_i)^2}{t(n-1)}}$$

wherein t represents the number of samples, n , the number of weeks in the analysis of replicates, \bar{x}_{ij} the average of duplicate samples at each week and sample, and \bar{x}_i the average results per sample (each week, the average of duplicate tests obtained in repeatability conditions, \bar{x}_{ij} is obtained)

Heavy metals	Relative intermediate precision
Copper	0,0381
Zinc	0,0387
Lead	0,0699
Chromium	0,1049
Cadmium	0,1238
Nickel	0,1084

Trueness

The trueness was assessed by comparing known and measured concentration of 6 reference materials. Then, the analyte recovery is estimated through equation 1.7.

$$1.7 \quad \bar{R}_m = \frac{\sum_i \bar{C}_{MR_i}}{t}$$

Wherein \bar{C}_{MR_i} represents the average concentration estimated from the analysis of the reference materials, i , C_{MR_i} the known concentration of MR_i and t , the number of reference materials.

To assess whether the results are affected by systematic effects that need correction, we used a t-test. It was only necessary to make correction for zinc. The initially estimated concentration is multiplied by $1/\bar{R}_m$.

Conclusion

The developed quality control strategy allows identifying the cause of deviations in measurement results (ex. contaminations or ICP-AES linearity response deviations) and involves checking the quality of the estimated measurement uncertainty. The sensitivity of ICP-AES is checked through the analysis of a standard solution with a concentration near the LoQ.