Characterization of metallic trace elements in soils by portable X-ray fluorescence spectrometry

Clément Rosière[1,*], Bruno Godin[2], Amandine Liénard[1], Gilles Colinet[1]

[1] *Gembloux Agro-Bio Tech University of Liège - Department BIOSystem Engineering, Soil-Water-Plant Exchanges*

Passage des Déportés, 2 - 5030 Gembloux - Belgique

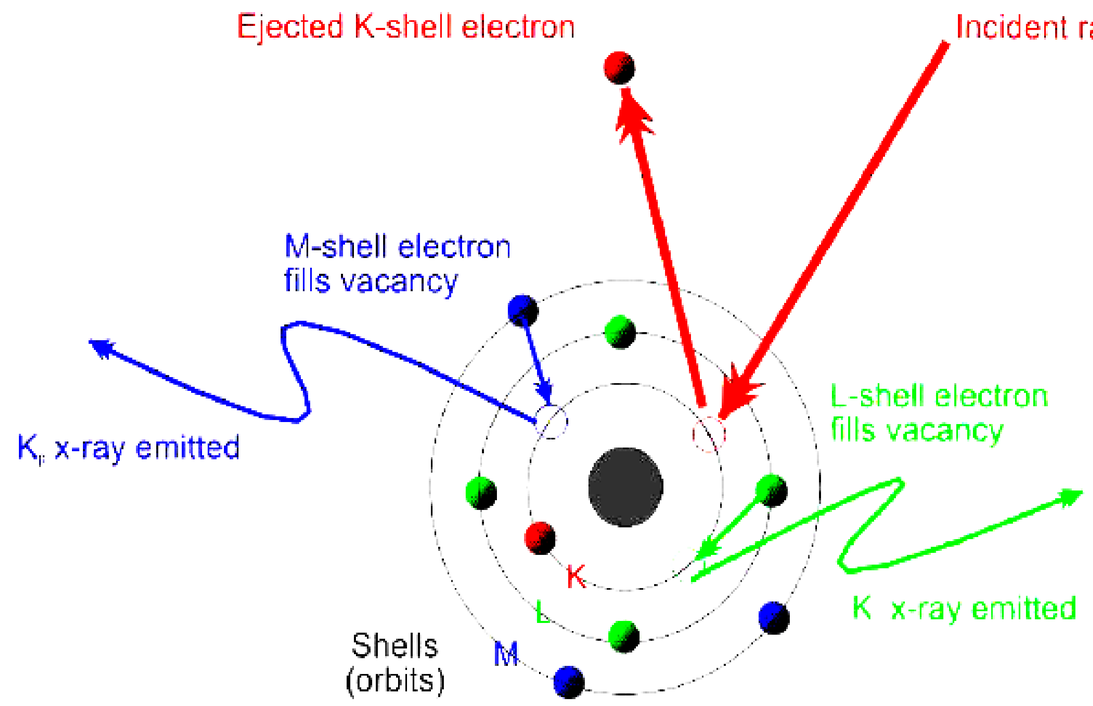
[2] *Walloon agricultural Research Center (CRA-W) - Valorisation of Agricultural Products Department*

Chaussée de Namur, 146 - 5030 Gembloux – Belgique

Corresponding email : clement.rosiere92@gmail.com

Introduction

- X-ray Fluorescence Spectrometry (XRF):
  - Simultaneous determination of mineral elements
  - Fast
  - Non-destructive
  - Inexpensive method
- This work focused on metallic trace elements determination (Cu, Zn, Pb, Ni, Cr and As) :
  - Subject to specific regulations for sewage and contaminated soil management.
- The reference method in those fields :
  - Aqua regia ($HCl+HNO_3$, ISO 11466) digestion followed by Atomic Absorption Spectrometry (AAS) or Inductively-coupled plasma atomic emission- or mass- spectrometry (ICP-AES/ICP-MS).
- Aqua regia digestion-based analysis :
  - Underestimates the total content of elements because it does not completely digest silicates, while XRF is supposed to measure total content.
- We compared the prediction values by XRF with the values from the aqua regia digestion for some reference values in soils.



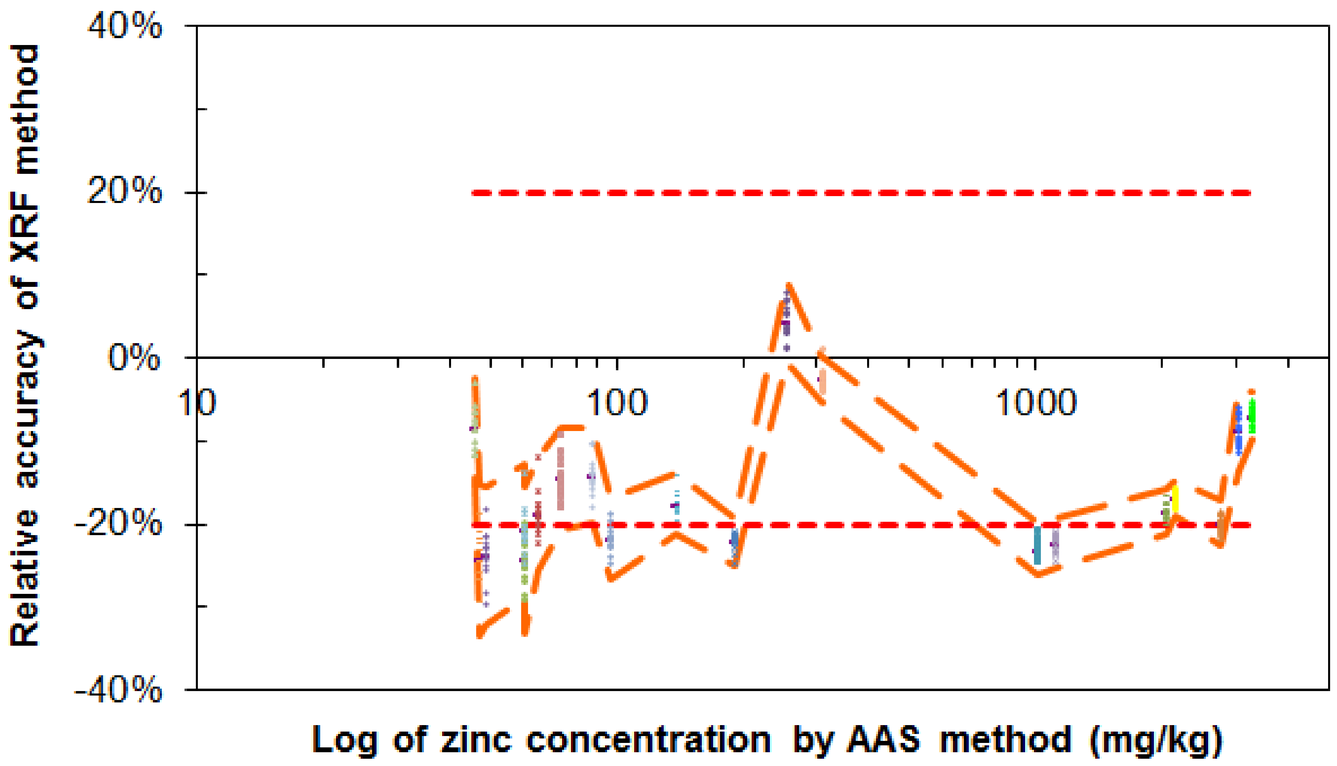
X-ray fluorescence phenomenon (Bruker)

Accuracy

- Seventeen soils (mainly agricultural soil) were analyzed by XRF (S1 Titan 600, Bruker) in a desktop configuration with XRF cells (Ø 40 mm, Prolene film 4µm)
  - → Compared to their current aqua regia digestion-AAS values.
  - → All samples were air-dried, sieved and crushed to 200 µm.
- In order to assess the measurement uncertainty of the XRF
  - → Accuracy profile method was chosen
    - Under intermediate precision conditions
      - 5 series
      - 3 repetitions per day,
      - 3 readings per measurement
- The accuracy profile allows :
  - →Determining an interval which will contain 95% of the measurements. This interval is then compared to an acceptability interval, which was fixed at ± 20% of the reference value, to vouch for the validity.

XRF (S1 Titan 600, Bruker) in desktop configuration

Zinc accuracy profile



Long dotted orange line: Tolerance limits

Short dotted red line: Acceptance limits

- XRF method underestimates the zinc content compared to the AAS method.
  - → A simple slope and intercept correction of XRF data could generally restore the trueness (bias) to improve the accuracy on a larger concentration range.
  - → Concentration levels close to detection limits have a higher degree of random variability because of the Horwitz curve.
- Strong linear correlations were found in soils for Cu, Zn or Pb ($R^2 > 0.99$) between pXRF and aqua regia digestion-AAS.
  - → The linear correlation was very poor for Cr, probably due to internal calibration issues.

Conclusions

- XRF → Interesting tool and easy to use for the prediction of metallic trace elements content in soils at a low cost.
  - → To predict reference values (aqua regia digestion-AAS method) with sufficient accuracy, direct measurements are not suitable and a specific XRF calibration is recommended. A simple linear regression is adequate to improve the accuracy of the measured values in some cases, depending on the wanted future application.

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