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# VALIDATION OF A METHOD FOR ACID TREATMENT AND SUBSEQUENT DETERMINATION BY ICP-OES OF HEAVY METALS IN SOILS AND INDUSTRAIL TALINGS

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## BACKGROUND

The most used precursors for producing of geopolymers are metakaolin, fly ash and granulated blast furnace slag. A large number of studies show that the mine tailings, whose utilization is an extremely important worldwide, are candidates for precursors for these new materials. The geochemical composition of wastes is crucible for the structure and physical properties of the newly synthesized material. The composition of mine wastes is not only with structural importance for geopolymerization process, but also from ecological importance, as a component of future wastes. The aqua regia digestion is not total digestion technique but is powerful method for digestion of all environmentally available elements with exception of that bounded in silicate structures, which are considered non-mobile in the environmental conditions. This method could be applied not only for fast assessment of the toxicity of mine tailings and the geopolymers on its base, but also for evaluation of the degree of encapsulation of hazardous materials.

## CONCEPT

An open aqua regia digestion method of mine tailings and fly ashes followed by ICP-OES measurement was validated for determination of As, Cd, Cr, Cu, Pb, Ni and Zn. The selected elements are noted in the European Commission standards for non-agricultural soils.

## MATERIALS AND METHODS

Method digestion: Approximately 1.2 ± 0.0001g of the solid samples were transferred to the glass Beakers and were wetted with about 10 mL of distilled water. A 5 mL of concentrated $HNO_3$ and 15 mL of concentrated HCl were added. The Beakers were covered with a watch glass and heated for 120 min without boiling to reducing the volume by half. The solutions were filtered with filter paper in 50 mL volumetric flasks. The filter paper was washed in the funnel with 5 mL of hot (~95ºC) HCl and with hot (~95ºC) distilled water. After cooling, the solutions were diluted to the mark with distilled water.

Validation: The method of digestion was validated by analyzing CRM trace metals sewage amended soil, CRM005-50G, Lot LRAC9532, Expiry date May 2024. The limits of detection and quantification were determined. Emission lines free from spectral interference were selected. Accuracy, repeatability, reproducibility were evaluated. Results are reported with their expanded uncertainty. The bias were calculated, and applicability of the method was assessed by z-score.

Analysis of wastes: The validated method of digestion were applied. The results are reported with their expanded uncertainty

## VALIDATION

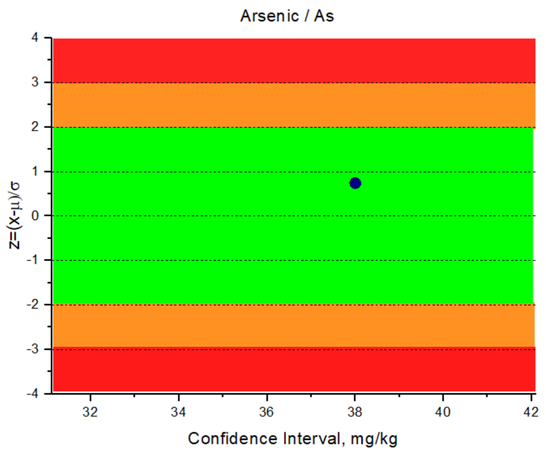
### Characteristics of the method measurements

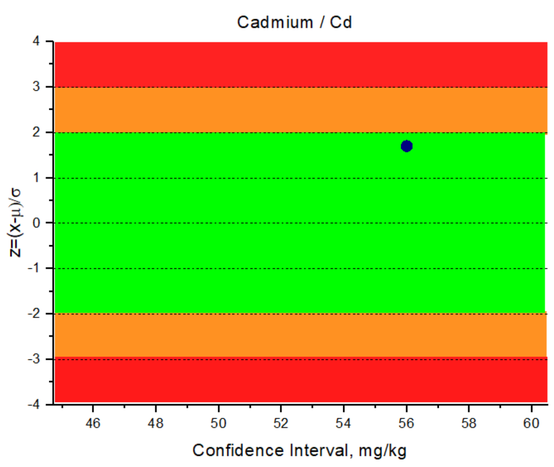
The limits of detection and quantification were determined after calibration and measurement the sample blank solution, accompanying sample preparation. The LOD=3SDbl and LOQ=10SDbl, where SDbl is the standard deviation of blank solution in mg/L, and then the LOD and LOQ are recalculated in mg/kg for 50 ml flask and 1.2 g sample weight. Calibration Interval, five points between 1 and 10 mg/L, axial view 30 sec, Power 1.2 kW; number of integrations 3; uptake 1.2 ml/min; Coolant 18 LPM; Auxiliary 0.5 LPM; Nebulizers gas flow 34 PSI.

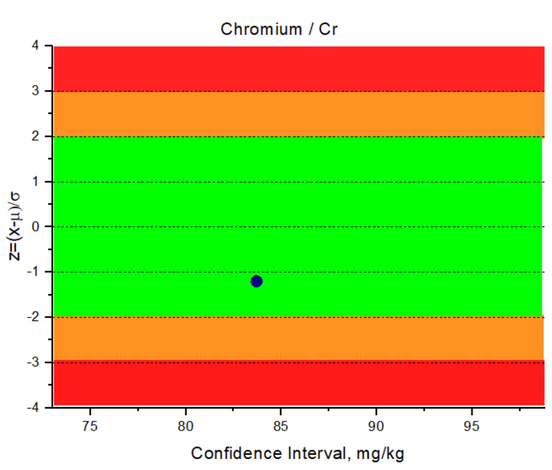
| Element | LOD mg/kg | LOQ mg/kg | Emission line, nm |
|---|---|---|---|
| **Arcenic/As** | 0.04 | 0.42 | 189.042 |
| **Cadmium/Cd** | 0.02 | 0.21 | 226.802 |
| **Cromium/Cr** | 0.04 | 0.42 | 205.552 free from Fe lines |
| **Copper/Cu** | 0.04 | 0.42 | 327.396 |
| **Lead/Pb** | 0.04 | 0.42 | 220.353 |
| **Nickel/Ni** | 0.04 | 0.42 | 231.604 |
| **Zinc/Zn** | 0.008 | 0.08 | 213.856 |

### Analysis of CRM trace metals sewage amended soil, CRM005-50G, Lot LRAC9532,

| | CRM certificate data | | | Analyzed CRM (10 rep.) | | |
|---|---|---|---|---|---|---|
| **Analyte** | Certified value±Expanded uncertainty, $mg.kg^{-1}$ | Confidence Interval | SD | Value ± Expanded uncertainty, $mg.kg^{-1}$ | SD | Relative bias, % |
| **Arcenic/As** | 36.6±1.9 | 31.11 to 42.09 | 5.49 | 38.00±1.2 | 0.60 | 3.8 |
| **Cadmium/Cd** | 52.6±2.0 | 44.71 to 60,49 | 7.87 | 56.00±0.8 | 0.40 | 6.5 |
| **Cromium/Cr** | 85.9±1.8 | 73.00 to 98.8 | 12.9 | 83.7±1.0 | 0.50 | 2.6 |
| **Copper/Cu** | 346±7.47 | 294.2 to 397.8 | 51.8 | 352.0±1.9 | 0.95 | 1.7 |
| **Lead/Pb** | 92.9±2 | 77.5 to 106.8 | 13.9 | 89.1±2.0 | 1.05 | 4.1 |
| **Nickel/Ni** | 54.3±1.6 | 46.16 to 62.44 | 8.14 | 51.4±2.1 | 1.05 | 5.3 |
| **Zinc/Zn** | 527±14.6 | 448 to 606 | 79.0 | 537±8.0 | 4.00 | 1.9 |



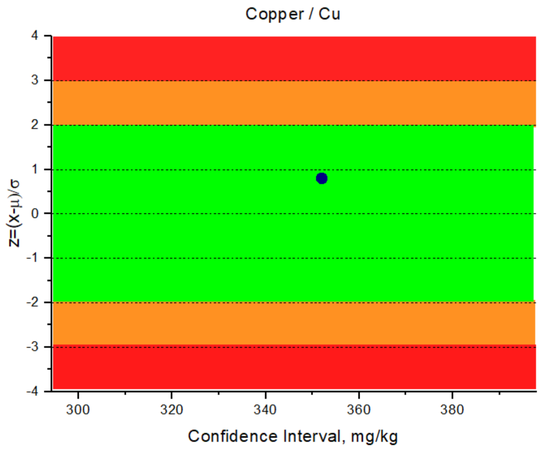

$$\text{zeta} = \frac{X_{\text{lab}} - X_{\text{ref}}}{\sqrt{u_{lab}^2 + u_{ref}^2}} \qquad bias\ (\%) = \frac{X_{lab} - X_{ref}}{X_{ref}} 100, \%$$

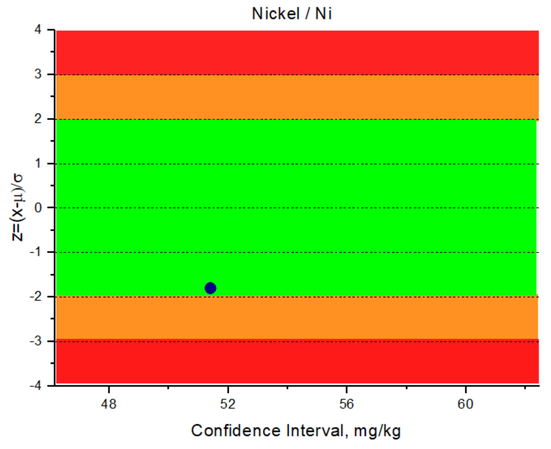
$u_{ref}$ = expanded uncertainty/2

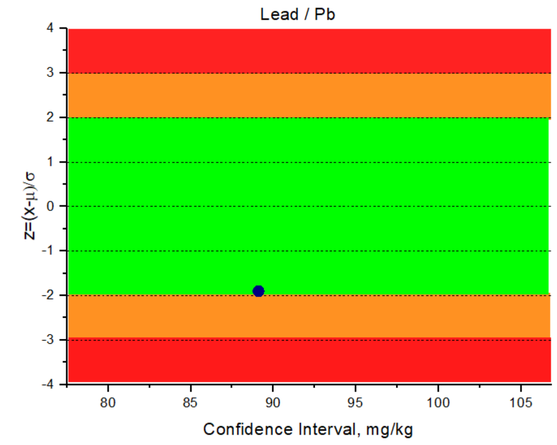
**|z| ≤ 2 satisfactory result**

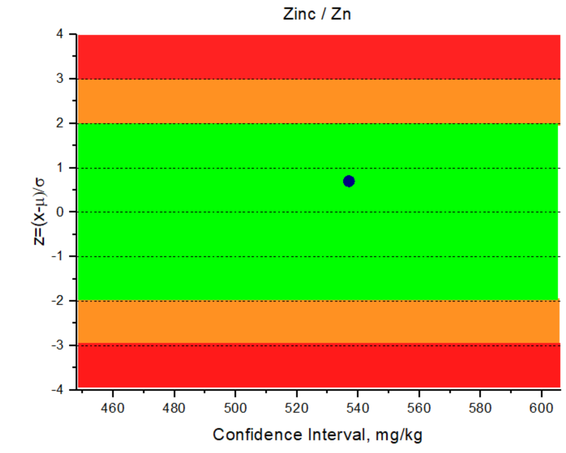
**2<|z| ≤ 3 questionable result**

**|z| > 3 unsatisfactory result**




### Calculation of uncertainties:

1. Uncertainty from repeatability

$$u_{(x_1)} = \frac{SD}{\sqrt{n}} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{mean})^2}{n-1}}$$

2. Uncertainty from analytical balance

$$u(x_2) = \sqrt{2.(m_1)^2} = 0.00008$$

$$m_1 = \frac{0.0001}{\sqrt{3}} = 0.00006$$

3. Uncertaintu from flasck clas A, 50 ± 0,060 ml

$$u(x_3) = \frac{a}{\sqrt{6}} = \frac{0.060}{\sqrt{6}} = 0.024$$

4. Combined root mean squareuncertainty
$u_i(x) = C_i.u(x_i)$, C=1

$$u_c(x) = \sqrt{u(x_1)^2 + u(x_2)^2 + u(x_3)^2}$$

5. Extended uncertainty $U=u_c.k$ (P=95%, k=2)

### RESULTS of the WASTES

| Element | Mine tailings | | | Fly ashes | |
|---|---|---|---|---|---|
| | AM mg/kg | 2364 mg/kg | 2365 mg/kg | BD mg/kg | M2 mg/kg |
| **Arcenic/As** | <0.42 | <0.42 | <0.42 | <0.42 | 1.20±0.57 |
| **Cadmium/Cd** | <0.21 | <0.21 | <0.21 | <0.21 | <0.21 |
| **Cromium/Cr** | <0.42 | 20.38±1.7 | 71.36±2.1 | 0.80±0.36 | 2.30±0.43 |
| **Copper/Cu** | 56.10±1.30 | 491.2±5.2 | 818.1±7.8 | 1.60±0.44 | 12.22±0.64 |
| **Lead/Pb** | 5.80±0.66 | 28.54±2.4 | 2444±11 | 1.90±0.58 | 9.40±0.84 |
| **Nickel/Ni** | 6.70±0.58 | 32.61±1.9 | 46.23±2.05 | 0.80±0.29 | 19.70±0.92 |
| **Zinc/Zn** | 2.70±0.36 | <0.08± | 195.0±2.0 | <0.08 | 2.60±0.71 |

## ACKNOWLEDGEMENTS

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