

Evaluation of Soil Mineralization Efficiency Using Microwave-Assisted Aqua Regia and Four-Acid Mixture

Bogdan Simion Angyus¹, Marin Șenilă¹, Anamaria Iulia Török¹, Erika Andrea Levei¹, Claudiu Tănăselia¹, Oana Cadar¹

¹National Institute of Research and Development for Optoelectronics INOE 2000. Research Institute for Analytical Instrumentation Subsidiary. Cluj-Napoca. Romania. bogdan.angyus@icia.ro

Introduction

Accurate elemental analysis of soils requires necessitates complete digestion of the sample. The present study compares Aqua Regia (AR) and Four-Acid mixture (HNO₃, HCl, HF, HClO₄ - 4A) for microwave-assisted soil digestion methods prior to ICP-MS, evaluating their relative performance across key trace elements.

Discussion

No statistically significant differences were detected between AR and 4A digestion for any of the six measured elements (Cr, Co, Ni, Cu, Cd, Pb) based on paired t-tests (p > 0.05). This indicates that, on average, both digestion methods produce comparable results for soil analysis.

AR exhibited to yield slightly higher concentrations of Cr, Co, and Cu in the majority of examined soils, (while 4A digestion recovered higher concentrations for Ni, Cd, and Pb in some samples). In the case of Ni, Cd, and Pb elements, 4A digestion resulted in enhanced recovery. These differences reflect the relative efficiency of the digestion reagents for different element matrices and the mineralogical composition of the soils.

Variability between soils was most evident for Pb, where certain samples exhibited AR/4A ratios above 2, suggesting that soil composition strongly influences extraction efficiency. The ratios for other elements were generally close to 1, indicating similar recoveries for both digestion methods. Both digestion procedures are suitable for routine ICP-MS analysis. Aqua Regia offers a simpler, widely used approach, while the 4A mixture can provide slightly higher recovery for elements resistant to single-acid attack, particularly in soils with complex matrices.

Conclusions

The application of both AR and 4A digestion methods has been demonstrated to yield comparable/analogous results for trace and major elements in soils. The variability observed in soil composition has a significant impact on recovery outcomes, with lead (Pb) exhibiting the greatest variability. The reliability of both methods for routine ICP-MS analysis is contingent upon the analytical purpose and target elements.

Experimental Procedure

Two microwave-assisted digestion methods were compared for soil sample mineralization prior to ICP-MS analysis.

AR Digestion - Soil samples (0.5–1.0 g) were treated with HNO₃ and HCl (3:9, v/v) and digested by microwave assistance. Final solutions were diluted to 100 mL.

4A Digestion- Soil samples (0.25 g) were digested with a mixture of HNO₃, HCl, HF, and HClO₄ (3:3:2:2, v/v/v/v) using a Berghof microwave system. After HF neutralization with boric acid, the solutions were filtered and diluted to 25 mL.

Table 1. Trace elements concentration after digestion using AR and 4A methods (mg/kg, dry weight -DW)

| | Cr (AR) | Cr (4A) | Co (AR) | Co (4A) | Ni (AR) | Ni (4A) | Cu (AR) | Cu (4A) | Cd (AR) | Cd (4A) | Pb (AR) | Pb (4A) |
|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Soil 1 | 27.3 | 18.6 | 41.4 | 27.9 | 17.4 | 15.1 | 9.7 | 6.0 | 4.2 | 4.2 | 90.1 | 102.7 |
| Soil 2 | 25.9 | 17.5 | 12.6 | 8.6 | 10.1 | 8.4 | 2.3 | 1.9 | 2.4 | 2.1 | 28.3 | 40.6 |
| Soil 3 | 18.1 | 13.3 | 5.2 | 3.8 | 5.7 | 5.7 | 2.2 | 2.0 | 1.8 | 1.6 | 16.1 | 4.2 |
| Soil 4 | 33.3 | 32.2 | 6.4 | 6.0 | 9.4 | 9.0 | 11.5 | 10.1 | 2.0 | 2.0 | 35.2 | 48.6 |
| Soil 5 | 3.9 | 3.8 | 27.0 | 28.7 | 5.9 | 7.3 | 3.4 | 3.9 | 0.8 | 0.9 | 46.0 | 17.2 |
| Soil 6 | 2.8 | 4.3 | 9.0 | 8.1 | 2.8 | 4.9 | 1.5 | 1.8 | 0.8 | 0.9 | 8.0 | 8.2 |
| Soil 7 | 3.5 | 5.2 | 2.8 | 3.3 | 2.0 | 4.7 | 1.4 | 2.0 | 0.7 | 0.9 | 6.1 | 7.7 |
| Soil 8 | 2.1 | 3.3 | 2.9 | 4.0 | 1.6 | 4.4 | 0.7 | 1.5 | 0.7 | 0.9 | 5.2 | 7.2 |
| Mean | 14.6 | 12.3 | 13.4 | 11.3 | 6.9 | 7.4 | 4.1 | 3.6 | 1.7 | 1.7 | 29.4 | 29.5 |

Table 2. AR vs. 4A: Paired t-test results

| Element | Cr | Co | Ni | Cu | Cd | Pb |
|---------|------|------|------|------|------|------|
| p-value | 0.18 | 0.26 | 0.43 | 0.43 | 0.70 | 0.94 |

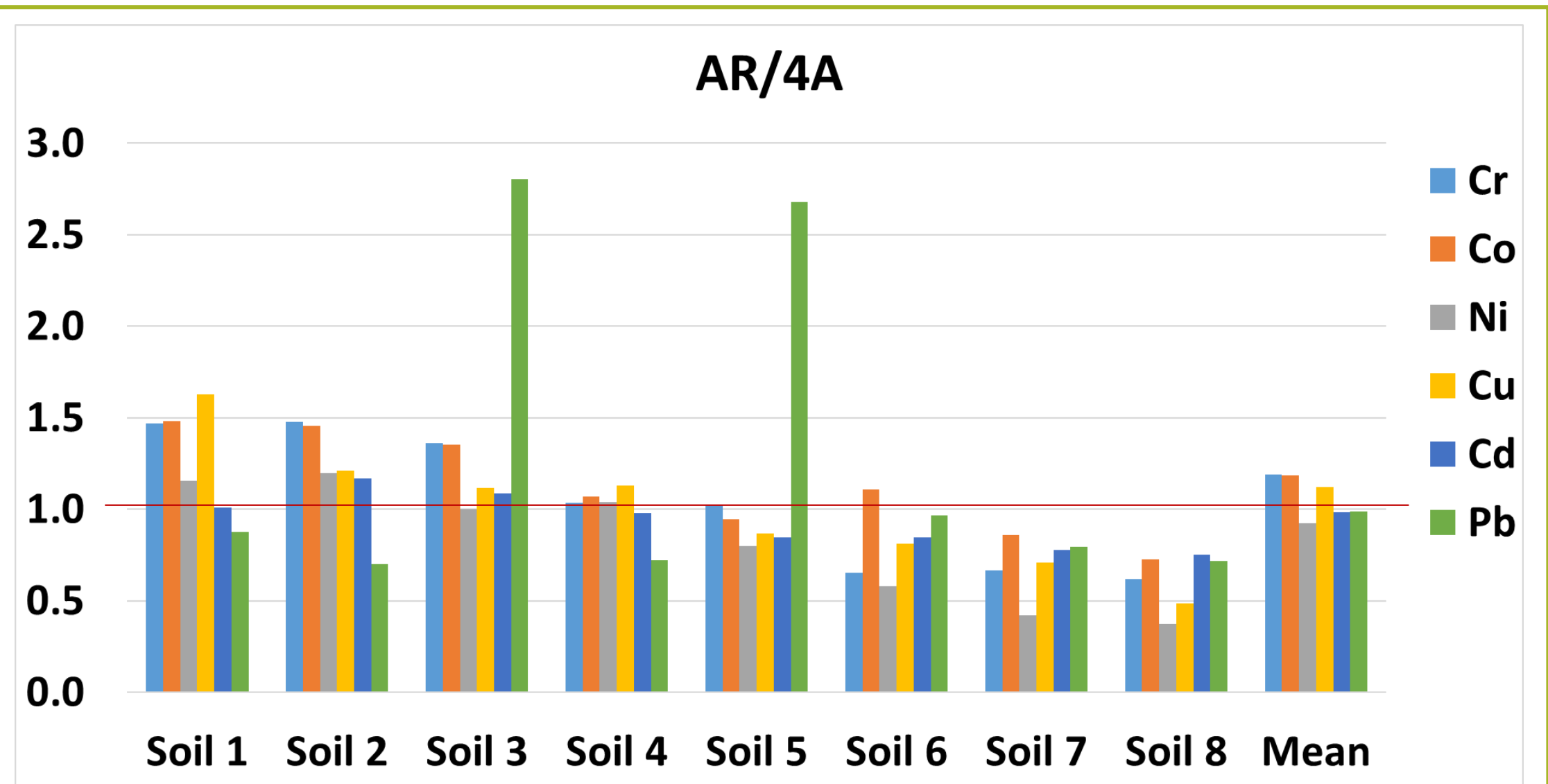


Figure 1. Ratio of results from AR to 4A digestion methods

Acknowledgements: This research was carried out through the Core Program within the National Research Development and Innovation Plan 2022- 2027, carried out with the support of MCID, project no. PN 23 05