

## ANALYTICAL POSSIBILITIES OF TOTAL REFLECTION X-RAY SPECTROMETRY (TXRF) FOR TRACE SELENIUM DETERMINATION IN SOILS AND LEACHING SOLUTIONS

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The geochemical cycling of selenium (Se) is an important issue for human health due to the narrow range between the nutritious requirement and toxicity effects upon Se exposure. To estimate its environmental impact, the study of the Se content and mobility in soils are of great concern. However, the determination of this element in soils and related solutions is challenging due to low concentrations within complex matrices that hamper the analysis in most spectroscopic techniques. In this work, we explored several analytical approaches combined with Total Reflection X-Ray Fluorescence (TXRF) for Se determination in soils and soil leachates, the latter using a case study of acid-rain soil interaction experiments.

In a first set of experiments, we studied the possibilities of direct analysis of soil suspensions and leachates by TXRF without any additional sample treatment. It was found that the direct analysis of soil suspensions using 20 mg of fine ground material (<50µm) suspended in 1mL of MilliQ water led to a relatively high Se LOD of 1 mg/kg (worldwide Se average in soils = 0.4mg/kg) and was therefore only suitable for seleniferous soils [1]. The direct determination of 10 µL of leaching solution led also to a Se detection limit (6.9µg/L) higher than the Se content in most natural samples. However, the direct TXRF analysis of leachates was attractive for lab controlled experiments due to the multi-elemental character and the low sample amount (10 µL) required [2]. Therefore, application to kinetic sorption studies of mass limited samples was possible [2,3].

To decrease matrix effects and improve the LOD for Se determination in soil digests and leaching solutions several fast and simple analytical strategies were tested. In the case of soil extracts, the application of a liquid-liquid extraction procedure using ethyl ether and the introduction of a Cr absorbent in the instrument configuration were carried out to avoid the associated problems on TXRF analysis of soil extracts due to the high Fe concentrations (~700mg/L). However, the more sensitive analytical strategy was found to be the application of a liquid-liquid microextraction procedure (DLLME) using APDC as chelating agent before the TXRF analysis of the soil digest. With such approach, the Se detection limit was 0.05 mg/kg that was comparable or lower than those obtained in previous works using other popular spectrometric techniques such as GFAAS, ICP-MS and AFS. The calculated Se concentration for JSAC-0411 certified reference material ([Se] = 1.32±0.27 mg/kg) using the combination of DLLME and TXRF ([Se] = 1.40±0.23 mg/kg) was in agreement with the certified value [1]. The same DLLME procedure was also studied as analytical strategy to improve the Se detection limits in leaching solutions (LOD: 0.7 µg/L). An additional advantage of the application of this procedure to this type of environmental liquid samples was the possibility to quantify inorganic Se speciation (selenite and selenate) in solution in a simple and inexpensive way, which is crucial to study the bioavailability, toxicity and transport in the environment [3].

It is expected that the application of the developed analytical methodologies based on TXRF will be useful to determine Se in soils and leaching solutions and, therefore, to improve the current knowledge on the Se behaviour in the environment.

### References:

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