Comparison of ^{238}U mass fraction measured by ICP–MS and Instrumental Neutron Activation Analysis techniques

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Introduction: Uranium is an element present in ambient air, water, soil and rocks [1]. The most abundant natural radioisotope of this actinide (^{238}U) produces in its chain decay the radionuclide ^{222}Rn [2], which is a tracer for atmospheric mixing and transport model validations [3]. The ^{238}U activity concentration in superficial soil samples is a crucial parameter for some ^{222}Rn flux map modeling methodologies [4].

Methods: In this study, 18 superficial soil samples were analyzed. The content of ^{238}U was assessed using two techniques: (i) by the comparative method of the Instrumental Neutron Activation Analysis (INAA) [5] and by ICP–MS (ELAN 6000, PerkinElmer) [6]. Certified Reference Materials (CRM) SRM 1646a Estuarine Sediment and USG STM–2 were used both as comparators in the INAA technique and to ensure quality control. The normality and homoscedasticity of the data were evaluated. Finally, the Mann- Whitney U test [7] was used to assess whether or not there is a significant difference ($\alpha = 0.05$) between the two techniques.

Results: The z-score was calculated to ensure quality control. Z-scores values was obtained by the Modified Horwitz Equation [8], which takes into account the order of magnitude of the content of the analyte and is independent of the CRM uncertainties, unavailable for the CRM used. The z-score values obtained ($n = 3$) for the radionuclide ^{238}U were 0.5 for the CRM USG STM–2 and -0.4 for SRM 1646a. The z-scores obtained are smaller than 2 therefore they are considered satisfactory [9].
Regarding the statistical parameters of the comparison between the techniques, the normality (Shapiro Wilk) was not verified ($p = 0.02$ for ICP-MS and $p = 0.03$ for INAA). The *p-value* for the test for equal variances (F test) was 0.71
Mann-Whitney U test was used instead of Student's test due to the non-verification of the normality parameter in the data. The *p-value* from the Mann-Whitney test (0.51) indicates that there is no significant difference between the ^{238}U content measured by the two techniques.

Conclusions: Statistical analysis showed that there is no significant difference between the ^{238}U mass fraction measured by the ICP–MS and the INAA – comparative method. In the future, certified reference materials will also be assessed by ICP–MS in order to corroborate this statistical comparison from a metrological point of view.

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