Tracing sources of uranium contamination using minor isotopes

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Isotopic signatures of uranium in environmental samples, including the minor as well as the major isotopes, can serve as highly sensitive tracers of environmental uranium contamination. Natural and non-natural sources of uranium contamination can sometimes be distinguished based on variations in the ratio of the major isotopes of uranium ($^{235}U/^{238}U$) because natural uranium has an essentially constant $^{235}U/^{238}U$ ratio, whereas processed nuclear materials are generally relatively enriched or depleted in ^{235}U. However, measureable variations in $^{235}U/^{238}U$ ratios occur only in response to relatively significant contamination with non-natural uranium, and mixtures of enriched and depleted uranium can sometimes be obscured. Isotopic ratios involving the minor isotopes of uranium including ($^{234}U/^{238}U$) activity ratios and $^{236}U/^{238}U$ ratios can serve as complementary and significantly more sensitive tracers of uranium contamination from processed nuclear materials in environmental samples. The presence of measureable ^{236}U, an essentially non-naturally occurring isotope of uranium formed by neutron-capture of ^{235}U in processed nuclear materials, is particularly diagnostic of anthropogenic uranium contamination. Tree bark, which effectively traps airborne dust and aerosols, serves as a natural repository of environmental contaminants, including uranium released to the environment during processing of nuclear fuel.

We have analyzed the major and minor isotopes of uranium in nine tree bark samples from southwestern Ohio in the vicinity of the Fernald Feed Materials Production Center (FFMPC), where estimates of inadvertant releases of uranium dust to the atmosphere between 1951-1985 range from 200,000 to 1 million pounds [1]. Our results show that tree bark as far away as 25 km from the FFMPC site contains measureable ^{236}U. Measured $^{236}U/^{238}U$ ratios increase progressively towards the FFMPC site, reaching ratios as high as 1.2×10^{-4}. In addition, ($^{234}U/^{238}U$) activity ratios in most samples are below one and exhibit a strong negative correlation with $^{236}U/^{238}U$, indicative of variable degrees of mixing between natural and depleted uranium, the latter enriched in ^{236}U from nuclear fuel reprocessing. Depleted $^{235}U/^{238}U$ ratios were only detected in the more contaminated samples closer to the FFMPC site, demonstrating that the minor isotopes are significantly more sensitive tracers of anthropogenic environmental uranium contamination.

[1] Makhijani (2000) *Inst. Energy & Environ. Res.* **5**(3).

Challenges facing the production of RMs for geochemical microanalyses

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The production of reference materials suitable for *in situ* microanalyses faces a number of challenges beyond those encountered for bulk sample applications. One obvious problem is the metrological requirement that RMs are only fit-for-purpose when using test portion masses at or above the levels for which the material's homogeneity has been confirmed. Worldwide no materials currently exist for which the chemical composition has been certified at the μm sampling scale [1]. With the exception of the International Association of Geoanalysts' protocol for the certification of geological reference materials [2, 3], the geochemical literature is largely silent about how this issue should be addressed. One approach is the characterization of a new material using bulk methods in conjunction with the homogeneity testing of the relative abundances of analytes using microanalytical methods. Such a strategy, however, is impacted by requirement that the intrinsic repeatability of the microanalytical method must be propagated to the expanded uncertainty assigned to the smaller test portion mass. Such an approach is unlikely to achieve the goal of an overall uncertainty which is no larger than 33% that of 'routine laboratory measurements' [2].

Only in rare cases is a direct determination of geochemical concentrations at sub-μg test portion masses metrologically possible (e.g. ion implantation in conjunction with SIMS depth profiling [4, 5]). Perhaps the greatest technical obstacle is the inability to determine the absolute mass of a test portion with low uncertainty – even the best of laboratory balances cannot determine a mass in the low μg range with an acceptable uncertainty. Here a method for crossing the μg-ng frontier is proposed. In contrast to using an isotopic spike for determining an element's concentration, a spike approach could conversely be use to determine a sample's mass in conjunction with assuming an absolute concentration for the given element in the material; large relative weighing uncertainties would thus be replaced by volumetric uncertainties associated with the spike solution.

[1] http://www. nano-refmat. bam. de [2] Kane *et al.* (2003) *Geostand. Newsletter* **27**, 227–244. [3] Kane *et al.* (2007) *GGR* **31**, 285–288. [4] Keppler *et al.* (2003) *Nature* **424**, 414–416. [5] Shcheka *et al.* (2006) *EPSL* **245**, 730–742.