

## Insights into Exploration Geochemistry (1): Four Acid vs. Aqua Regia Digest?

When you plan and budget for a geochemical sampling programme, you should ask yourself the following questions (excerpt):

- Aim and layout of programme
- Preparation and Digestion: none vs. Four Acid vs. Aqua Regia Digest vs. fusion
- ICP vs. (p)XRF
- Full vs. restricted element (e.g. U suite – U, Th, Nb, Ta) suite?
- Detection limits
- Cost

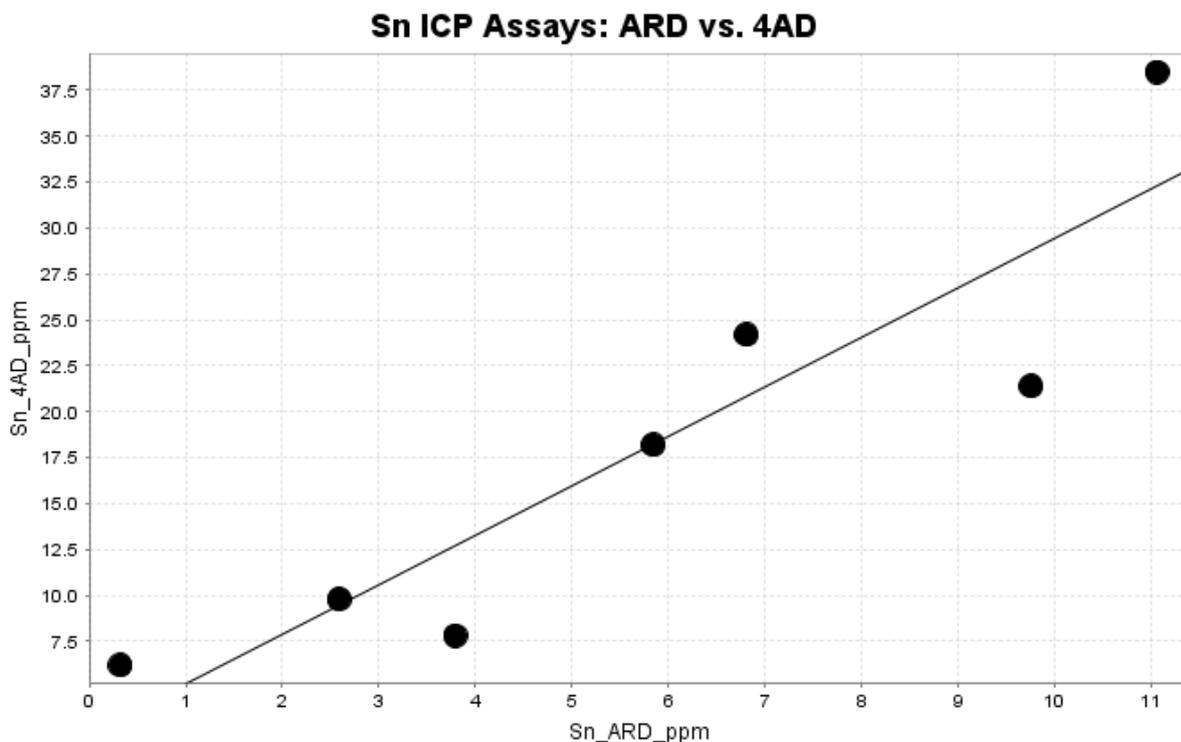
These topics and more are covered in my lectures and [workshop](#) “Advanced Mineral Exploration Geochemistry: Best practice industry methods and workflows”, available to students and professionals alike.

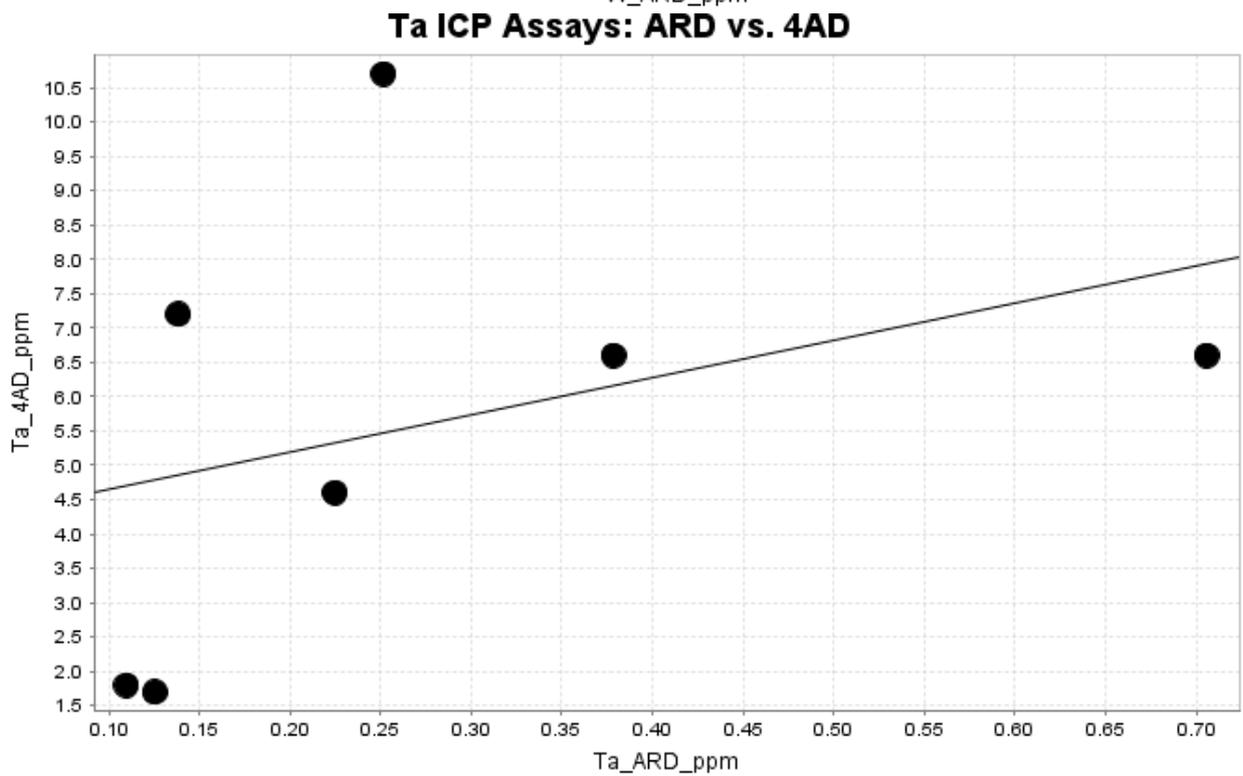
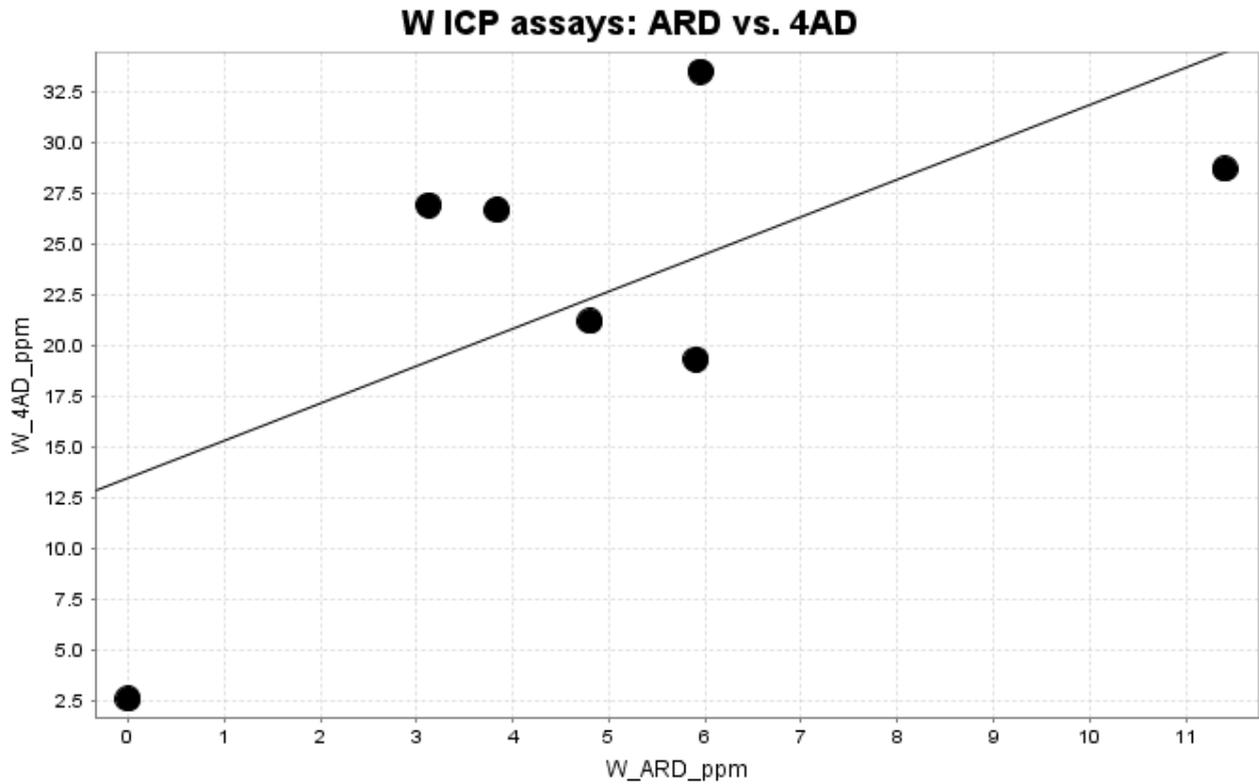
Considering and reviewing the analytical digestion options is very important and may have a considerable impact on the overall assay results and costs. Most commonly, geological samples undergoing chemical analysis either are **not digested** (‘dry’ geochemistry, e.g. XRF) or **partially dissolved** in acid of variable strength (‘wet’ chemistry) or **completely dissolved** (fusion, precious metals). The break-down of minerals in acid results in the release of elements into solution followed by multi-element analysis, such as ICP-MS or -OES. The important point to take away is that ‘dry’ chemistry will not liberate elements from the mineral lattice and therefore may underestimate elemental concentrations.

Traditionally, companies and governmental geological surveys have relied on the use of Aqua Regia digest for regional grassroots exploration. **ARD** is a weak digest comprising a mixture of nitric (HNO<sub>3</sub>) and hydrochloric acid (HCl). It allows to dissolve most sulphides, oxides, gold and platinum, however is not strong enough to completely break down quartz, zircon and heavy minerals, such as wolframite and cassiterite. Due to its simple application, ARD is a fast

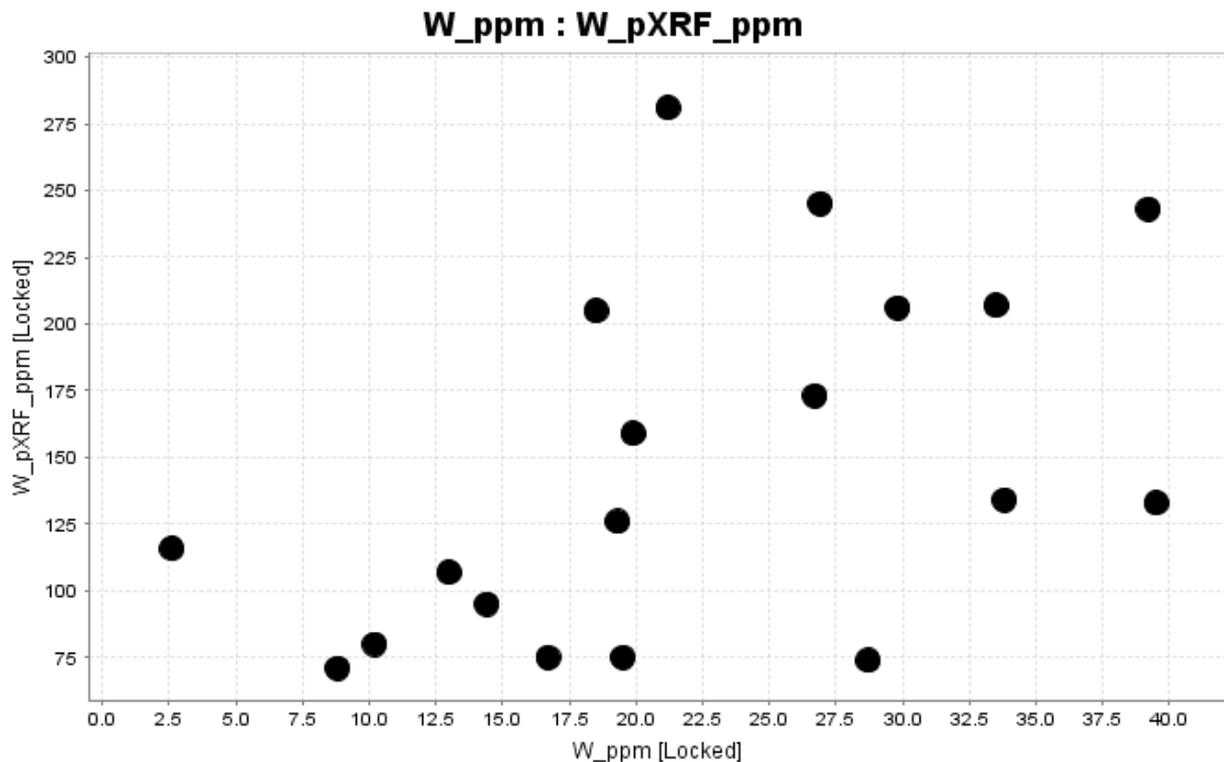
and cheap process. **Near-total or Four Acid Digest (4AD)** on the other hand is a stronger, yet more expensive, combination of HCl, HNO<sub>3</sub>, HF (hydrofluoric acid) and HClO<sub>4</sub> (perchloric acid). 4AD is a very effective dissolution package for multi-element analysis at trace levels of detection. This becomes crucial when establishing pathfinder vectors to covered orebodies, e.g. porphyry deposits. However, it needs to be noted that some refractory or resistant minerals (e.g. zircon, silica which is lost as SiF<sub>4</sub> gas) are only partially digested and that there can be a loss of volatile elements (e.g. As, Pb, Sb). This has adverse implications on the abundance of Zr and some heavy REE hosted in zircon.

I would like to illustrate this using stream sediment data from an area in France that I consider prospective for Sn-W and LCT deposits. The graphs below show clearly that ARD is under-reporting the values for Sn, W, Ta which are hosted in resistant minerals, namely cassiterite, wolframite and tantalite. This is because ARD is too weak to fully dissolve these minerals. Instead, assays obtained from 4AD are **commonly half a magnitude** higher than ARD and allow to distinguish anomalous from crustal abundance values.





However, compared to 'dry' pXRF assays, the 4AD still is under-reporting W values. This situation can be avoided by using fusion, however fusion is expensive and produces higher detection limits for key trace pathfinder elements required for additional petrogenetic studies.



My choice for exploring such deposits will be a compromise between pXRF coupled with ICP 4AD, even though fusion using metaborate flux may be a valid, yet, expensive and overall problematic option.

So, which package is the best for an exploration project? My answer is: It depends on the deposit and regolith type, elements of interest and what your overall aims are. If you are looking into getting a fast and cheap result and do not mind that the digest potentially does not extract a sufficient amount of the element of interest, then ARD is your choice. If you are interested, however, to use your trace element data to map lithology, alteration and mineralogy, then 4AD should be your choice.

So what technique applies to your project?

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