

A COMPARISON OF HYDROGEOCHEMICAL SAMPLING METHODS

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Recent hydrogeochemical sampling in the NE Yilgarn Craton, W.A. has tested various methods. Filtration sizes of 0.1 and 0.45 μm were compared for selected major and trace elements, while anion and cation exchange resins were also tested and compared to the exchange capacity of activated C for unfiltered samples, with the goals of improving detection limits and developing a “fieldy-proof” technique for industry groundwater exploration. Eleven samples were tested for the filtration comparison, while 28 samples were used for the assessment of the exchange resins and activated C. Previously, more than 100 samples have been collected using the activated C in the NE Yilgarn Craton.

A major concern is relating results between the different filtration sizes if standard filtration was not used in a hydrogeochemical exploration program. Clay minerals are often much smaller than 0.45 μm and theoretically could pass through the filter and adsorb metal in solution prior to analytical determination or release elements on acidification. A comparison between 0.1 μm and 0.45 μm filtration was conducted on 12 samples from the Honeymoon Well region. Often 0.45 μm filtration is considered the standard, primarily due to it being the minimum pore diameter size filter papers commonly available at the time of production of such standards. Smaller diameter filtration paper is now readily available.

No significant difference between the 0.45 and 0.1 μm filter size was found for major anions (Cl , SO_4) and cations (Na , Mg , K , Ca), as well as U , Mo and Si (Figures 1 and 2). Student’s t-test was used to determine significant differences. Correlations between the two treatments were very strong ($R^2 > 0.99$) and the slope of the line of best fit was very close to 1. Limited results for V , W and Cu and, to a minimal extent, Ni and Zn did not demonstrate significant advantage to using the finer, more expensive filter (Figure 2). However, Al and Fe show variable sample concentrations. Iron is not consistently higher or lower i.e. there is no consistent difference between treatments (Figure 2 and 3). There is no clear relationship between Fe and Al , i.e. if Fe is higher than expected, Al may not be higher for the same sample and filtration type (Figure 3). Aluminium concentrations are a little higher in the 0.1 μm filtration, which does not support the idea that small clays (aluminosilicate minerals) are getting through the 0.45 μm filter and being caught by the 0.1 μm filter.

In comparison, the near-perfect correlation between filter sizes for Si (Figure 2) relates to much higher dissolved Si and indicates the Si concentration is not influenced by the comparatively small concentrations of Al and Fe silicates that may pass through the filter membranes. The lack of significant difference between filter sizes for the trace elements suggests trace elements concentrations are not influenced by Al and Fe . In other words, Al and Fe do not dilute or concentrate the dissolved trace metals. The use of either tested filter size may well be acceptable for groundwater exploration in the NE Yilgarn, but further study of Fe and Al from the two filter sizes is required to fully assess the implications for groundwater studies in the other areas of the Yilgarn. At this stage the Fe and Al “dissolved” concentrations should be interpreted carefully in such neutral/fresh groundwater.

Carbon sachets have been routinely used for Au analysis, although this can be extended to Ag , Pd , Pt , U , W and other metals. The use of C extracted W and Pt has been useful as a vector to Ni mineralisation. The C sampling is unfiltered, easy to use, and may be more applicable to the mining and exploration industry hydrogeochemical sampling. The exchange resins have not been fully evaluated, but at this point do not seem as effective as the C . Direct measurement (ICP-MS/OES) of filtered and acidified samples is still generally the best option, but detection of PGEs is not possible and the activated C is preferred if PGEs are a key pathfinder. Activated C also offers a more resilient (“fieldy-proof”) sampling method.

Two forms of exchange resins were tested along with the activated C . The metals extracted from the anion exchange resin (Dowex MAC-3) were often below detection, with the two exceptions of U and W . The cation exchange resin (Aquasonic toxic metal sponge) extracted metals were commonly below detection, however Cr , Fe , Ni , Pb and U were detected in numerous samples.

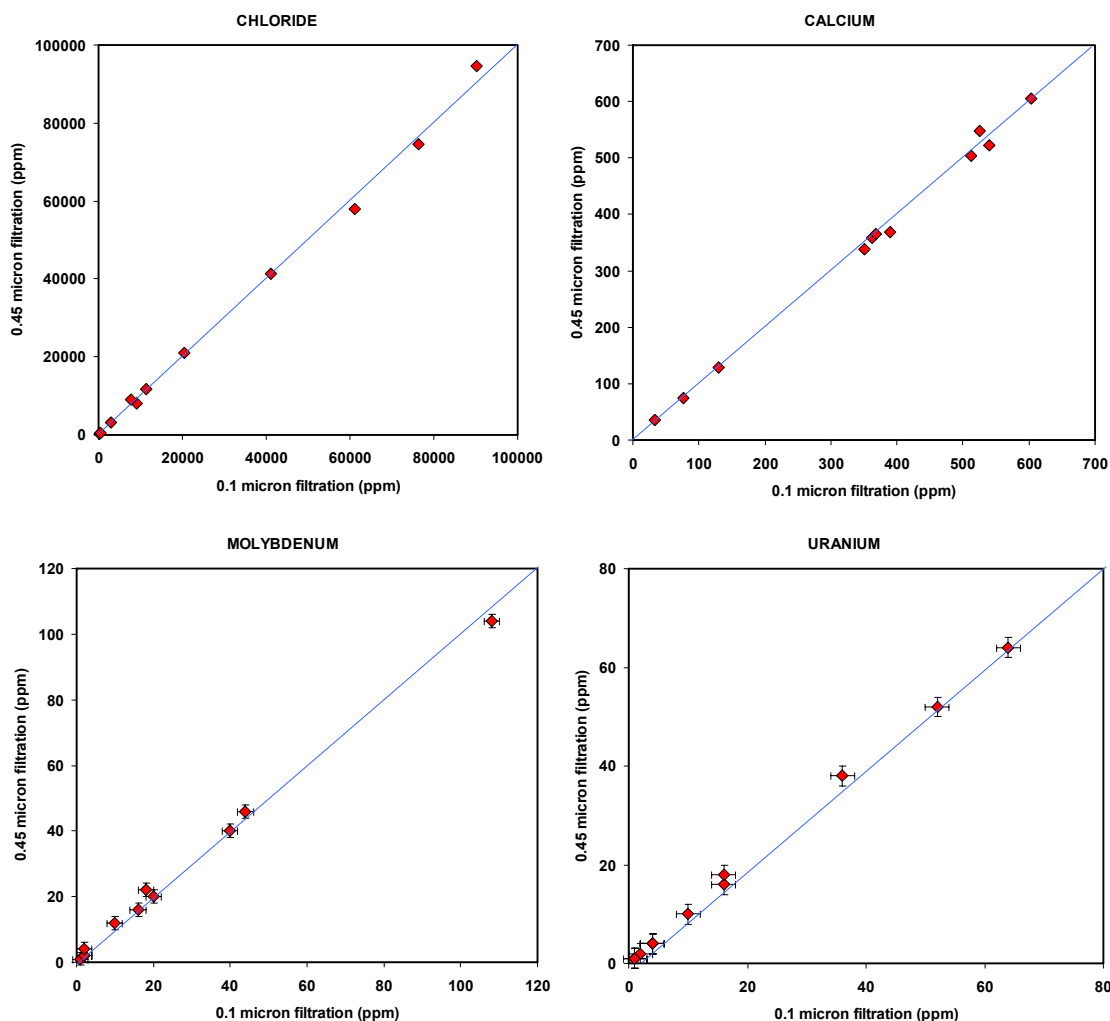


Figure 1: Chloride, Ca, Mo and U compared from the 0.1 and 0.45 μm filtration treatment methods. The blue line represents the perfect correlation and with no differences between filtration. Error bars are applied based on the detection limit of the analysis.

Uranium was measured for both exchange resins, C and via direct measurement. Although direct determination is considered the best technique, there is some agreement between the techniques. Uranium concentration agreement between the direct measure and the anion exchange extractable U was very good. The resins did not improve the detection of PGE, which is a major limiting factor in using hydrogeochemistry and PGEs as an exploration method. Activated C had better agreement with direct determination, and lower detection limits for PGEs. Correlation of the direct measurement (ICP-MS/OES) with the cation exchange resin was poor for Cr, Fe and Pb.

Assessing preferential sorption of metals was tested by applying all three methods simultaneously to the same water sample and comparing to the single method. Metals were adsorbed more by the resins and C that were not competing for exchange sites (individual method solutions). The anion exchange resin out competed the cation exchange resin for Ag, while the carbon removed far more Ag in the limited sample set. The anion exchange resin adsorbed more W than the carbon, indicating the anion exchange resins may be a better sampling method if W is the primary pathfinder. The preferential sorption of U and W on the anion exchange resin is expected given that these two elements form mobile oxyanions (e.g. $\text{UO}_2(\text{CO}_3)_2^{2-}$ and WO_4^{2-}) in the neutral waters of the NE Yilgarn. The cation exchange resin removed less Ni than the carbon sachet and is probably not adding value for Ni exploration compared to the activated C. A major advantage of the carbon is to get results of both negative and positive charged ions, even if the values are lower than other methods i.e. anion exchange of W.

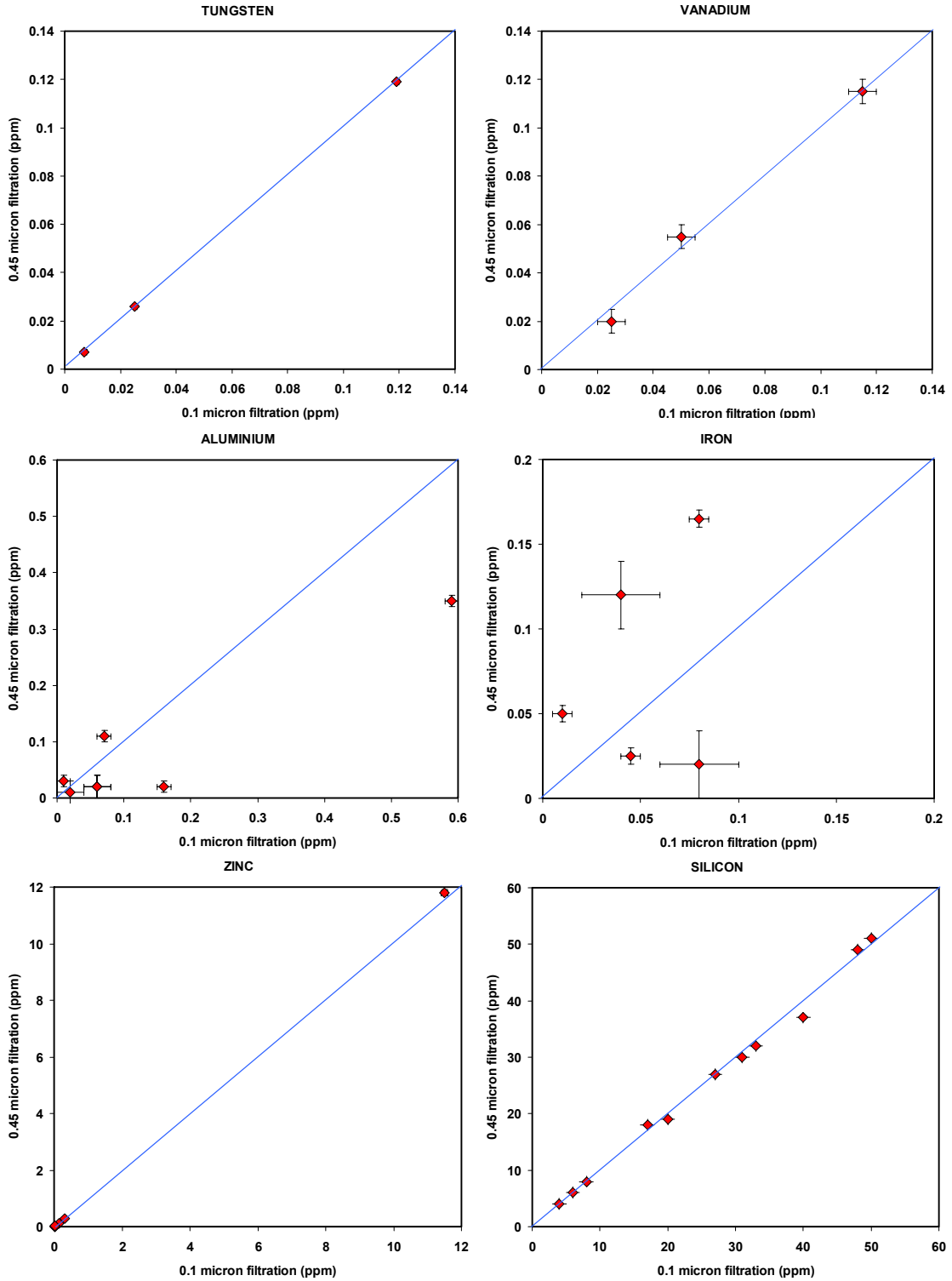


Figure 2: Tungsten, V, Al, Fe, Zn and Si compared from the 0.1 and 0.45 μm filtration treatment methods. The blue line represents the perfect correlation with no differences between filtration. Error bars are applied based on the detection limit of the analysis. Results were excluded where the concentrations were at or below the detection limit.

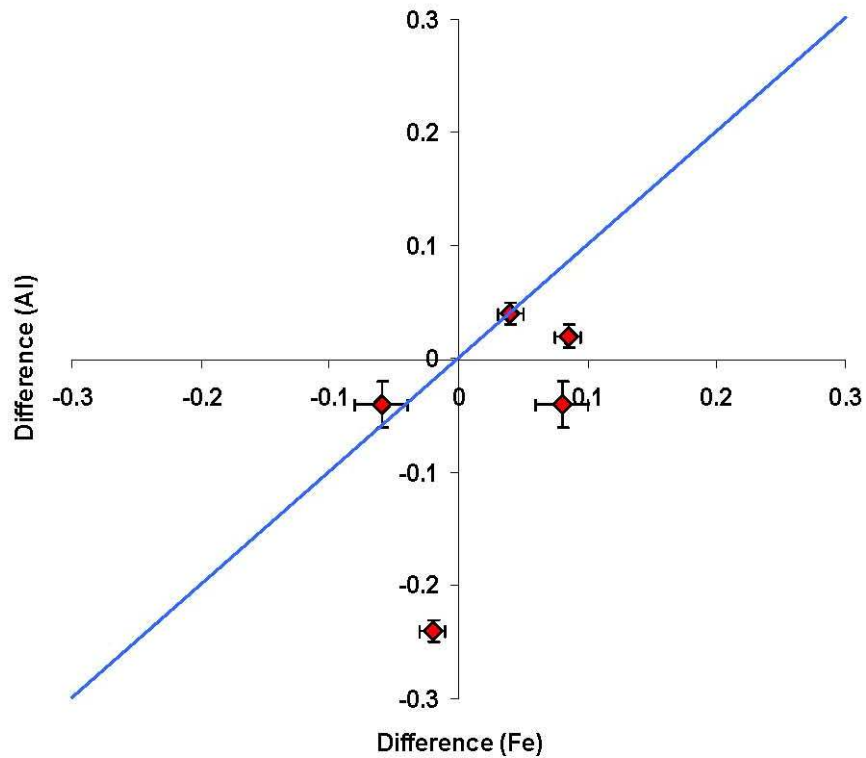


Figure 3: The difference between Al and Fe from the line of perfect correlation. The blue line represents relative consistent differences i.e. where the difference between the two filtration treatments for Fe was higher than expected, Al differences were also higher. Error bars are applied based on the detection limit of the analysis.

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