

Hydrogeochemistry for mineral exploration in Western Australia (I): Methods and equipment

INTRODUCTION

The use of hydrogeochemistry for mineral exploration is increasing worldwide. Here in Western Australia, and developing in eastern Australia, junior exploration companies regularly approach us to obtain a relatively straightforward method description to conduct hydrogeochemical sampling. Although there are numerous and varied approaches for hydrogeochemical exploration available these are not easily found in the literature (e.g. Giblin 2001; Taufen 1997) or can be complex to breakdown for simpler exploration needs (i.e. EPA-type reports). To address this need we have compiled a general methodology, some basic steps (that are not regularly published as it is “common” knowledge – to hydrogeochemists) and required equipment that has been successfully applied to groundwater sampling by CSIRO in Western Australia.

Leybourne & Cameron (*in press*) have also recently put together a thorough and available article on the use of groundwater for geochemical exploration. Many of the sampling and analytical techniques overlap, but Australian arid and semi-arid terrains require adjustments in the methodologies of Leybourne & Cameron (*in press*), Giblin (2001) and Taufen (1997) or at least a different understanding of the limitations for hydrogeochemistry in these environments. Much of Western Australia has a thick regolith cover (10s of metres of transported and residual weathered material) and varied depths to the water table (~2 to 80 m). The groundwater can be relatively fresh to hypersaline, with pH ranging from 3 to 9 (Gray & Noble 2006). Even the agricultural regions of Western Australia have some extreme acid and saline groundwater chemistry, as documented by Shand *et al.* (2009). These conditions can make sampling, analysis and comparison to other groundwater data potentially problematic. This paper presents the methodology of groundwater sampling in Western Australia whereas Noble *et al.* (2010) apply the methods in case studies at various sites. This article, along

with the previous references, should enable most industry explorers (with limited hydrogeochemical background) to develop a successful groundwater exploration program.

EQUIPMENT AND METHODOLOGY

Types of samples

Numerous practical options are available for collecting groundwater. Each option has advantages and disadvantages (Table 1). Farm water, water monitoring and exploration drill

Table 1. Groundwater sample site types with advantages and disadvantages of each.

Sample site type	Advantages	Disadvantages
RC/RAB type drill hole	Commonly available in the exploration area of interest	Potential for contamination, often not cased and may close or collapse shortly after drilling
Diamond type bore hole	Commonly available in the exploration area of interest, well cased and preserved	Commonly deep groundwater systems, generally cased to significant depth and not easily compared to other shallow samples*
Windmill	Easy access, no drilling costs	Potential for contamination if not regularly flowing, restricted available sample sites, shallow groundwater systems only
Water bore	Easy access, contamination unlikely	Uncommon, mainly shallow groundwater systems (with exceptions in areas dominated by deep water sources such as the Great Artesian Basin)
Monitoring bore	Easy access, contamination unlikely	Uncommon, shallow groundwater systems only
Open well	Easy access, no drilling costs	Potential for contamination if not regularly flowing, restricted available sample sites, shallow groundwater systems only

* If slotted, straddle packer system (Leybourne *et al.* 2000) could be employed to isolate groundwater flow at different depths to reduce decrease this disadvantage. This has not been tested in Western Australia.

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holes (also termed “bore holes” or “bores”), and open wells are all suitable for sampling groundwater, however, detailed notes, sample preparation and data interpretation are required. Comparing similar sample types is critical. In much of Australia the lack of available springs and seeps means this type of sample has limited use.

Basic Equipment

Water collection

Table 2 shows groundwater sampling methods and some of the advantages and disadvantages of each. Bailers (Table 2, method #1) are commonly employed for rapid retrieval of water samples. Numerous types are available and clear plastic disposable types are ideal for vertical bore holes.

Disposable bailers can be reused with care and cleaning. Other heavier types (with stainless steel end caps that house the valves) can be used, particularly for angled drill holes. The added weight ensures the sample is taken from the desired depth.

Figure 1a shows two bailer types and size (one is the heavier stainless steel ended 40 mm diameter bailer with rubber flow through valves and the other is a 19 mm diameter, plastic disposable bailer that uses a plastic ball to stop water backflow). Ideally, the retrieval cord has depth markings on it to gauge water table height and sample depth (Giblin 2001), but this is not required if a depth probe is used.

Buckets and direct sampling (Table 2, method #2)

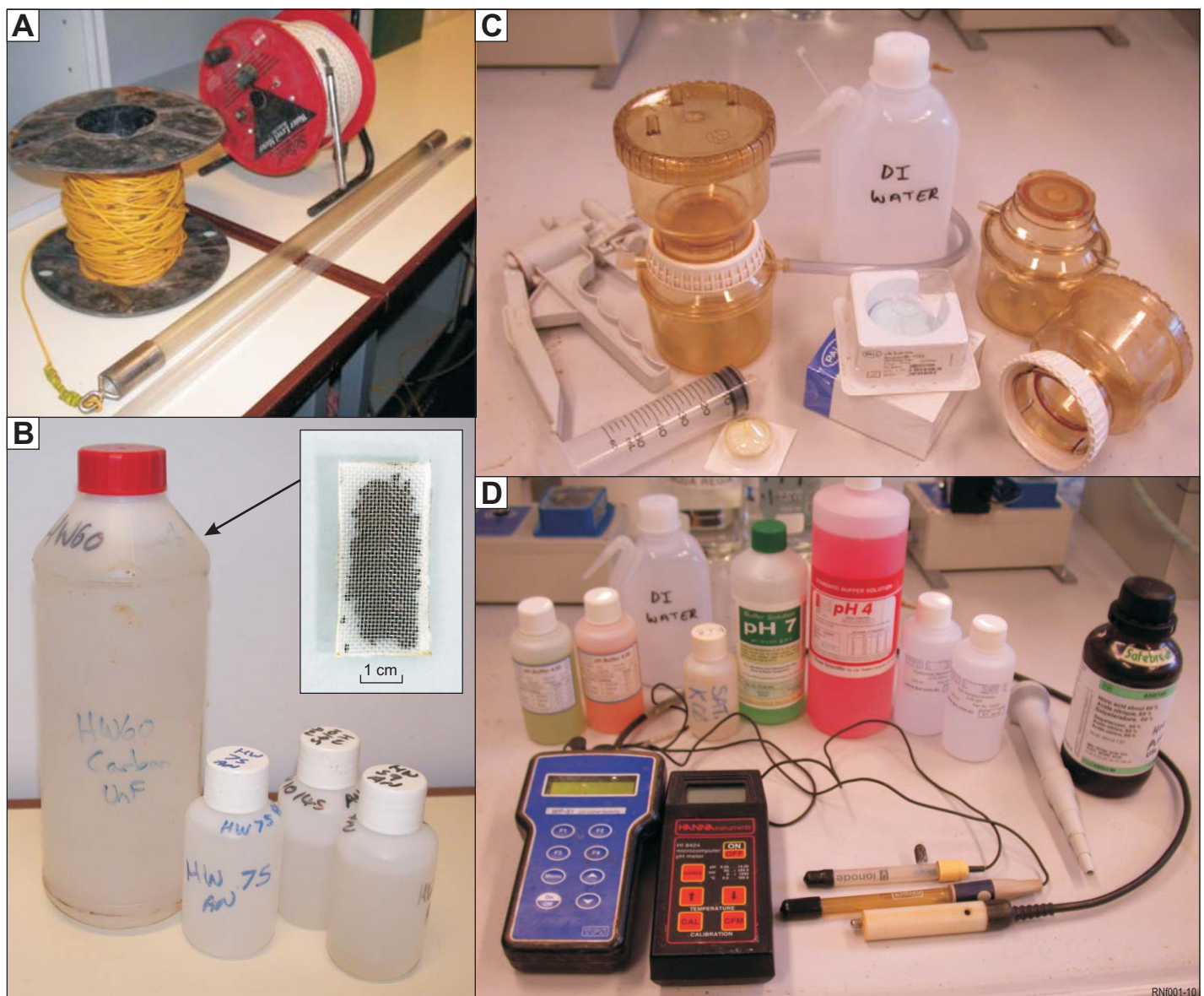


Figure 1. Typical sampling gear required for groundwater sampling; a) example of bailers (with polychain cable on reel) and a dip probe for depth measurement; b) water sample bottles and activated carbon sachet (inset); c) commonly used filtration equipment for water sampling*; d) meters, probes, variable pipette and solutions required for groundwater sampling. Solutions include pH buffer, saturated KCl, distilled/DI water, conductivity check solution and high purity HNO_3 .

*Rubber plunger on syringe pictured is not recommended for trace metals analysis due to Zn contamination. All plastic plungers are available.

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Table 2. Groundwater sampling methods with advantages and disadvantages of each.

Sampling method	Advantages	Disadvantages
1. Direct bailing from bore holes	Quick and portable, mostly applicable for exploration	Potential for contamination, interaction of groundwater with surface water, soil, air
2. Windmill sampling directly	Quick and only a bucket is required for collection, applicable for exploration and generally research	from outflow Potential for contamination, restricted available sample sites, shallow groundwater systems only
3. Pumping (3 bore volumes) with flow through cell for measurement	Very consistent results, applicable for research	Very slow, pumping equipment is not as portable, more equipment required. Unless drill hole is properly prepared, significant mixing of aquifers

from actively pumping farm bores and windmills are an effective way of sampling, but not always available in areas of interest. Pumps (Table 2, method #3) can be employed, providing the most representative results, particularly if at least three bore volumes are removed initially and a flow through measuring device is used i.e. the freshly recharged groundwater is measured as it is *in situ* with no atmospheric contact. While valuable in some studies, the time commitment to hydrogeochemical sampling in this mode is not practical for exploration and will not be discussed. Other options for more portable pumps and comparison to bailers are discussed by Leybourne & Cameron (*in press*) and Leybourne *et al.* (2000).

Water bottles and general equipment

High density polyethylene (HDPE) bottles are commonly used and suitable for groundwater samples (Hall 1998; Reimann *et al.* 1999; U.S. E.P.A. 1983), but these should be monitored using blanks to ensure no contamination occurs from the plastic (Reimann *et al.* 2007). Two sizes are used by CSIRO for sampling in Western Australia; 125 mL for the measurement of cations, anions and alkalinity and 1000 mL for the measurement of Au and PGEs (Fig. 1b). Other ancillary equipment is documented in Giblin (2001 Appendix 1).

Filtration gear

A variation on the method of Giblin (2001) is that field *continued on page 5*

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filtration is necessary for collecting the most representative “dissolved” fraction of elements. Cameron *et al.* (1997) determined filtration was unnecessary in Canadian surface waters that have very little particulate matter, but in semi-arid Australia the large quantities of sediment and organic debris that is frequently present in bailed samples need to be filtered out immediately.

Commonly the term “dissolved” refers to the water and its constituents that pass through a $<0.45\ \mu\text{m}$ filter membrane (Hall *et al.* 1996). Some clays and colloids are much smaller than this and will be analysed as “dissolved”, but minimising the interference from larger solids is desired. As discussed later, there is little difference between 0.45 and $0.1\ \mu\text{m}$ filtration for all elements tested, except Fe and Al. Multiple options for filtering water samples exist. The commonly available Nalgene® units of 250 mL capacity are ideal for most exploration projects. The filter unit uses a mixed cellulose, nitrocellulose or polyethersulphone filter paper (all of which are suitable). The pore size should be $0.45\ \mu\text{m}$ or less and the filter diameter is dependent on the unit size. A comparison of two filter pore sizes is documented later. The unit shown in Figure 1c requires 47-50 mm diameter filter papers. A pump is required with these filter units to ensure filtration is not overly time consuming. Other options include syringe filters that attach to a syringe which then provides positive pressure to filter (Fig. 1c). Syringe filters are best used for small volume sampling ($<50\ \text{mL}$). All-plastic syringes should be used as the rubber parts used in some syringes contain significant quantities of Zn and can contaminate water samples.

Field measurement equipment and chemicals

Essential field measurements for groundwater include pH, Eh and temperature. Electrical conductivity (EC) is beneficial, but can also be done in the laboratory later. Alkalinity measurements can be done in the laboratory for convenience if the sample bottle is properly sealed and there are low dissolved concentrations of elements such as Fe and Al. These elements can oxidize, generate acid and following neutralization of this acid by consuming bicarbonate, lower the alkalinity concentration from that of the original groundwater conditions.

Some pH/mV and conductivity electrodes and meters have a specific range of measurements, so it is important to ensure the equipment is suitable for the sampling area. For example, sampling in southern Australia requires conductivity meters that can measure up to $200\ \text{mS/cm}$. The electron potential or redox electrodes (Eh) are effective in Western Australian groundwater where the Fe^{2+} and Fe^{3+} couple are the dominant redox sensitive ions. The use of Eh measurements should be interpreted with care, and in other regions obtaining useful and stable Eh measurements is not possible. Measurement error is commonly $10\text{--}100\ \text{mV}$, which across a potential range of greater than $1200\ \text{mV}$ is still acceptable in obtaining information of the groundwater characteristics (e.g., Fe oxide, Mn oxide or sulfide dominated). The Pt electrodes have proven to be robust in measuring groundwater in semi-arid and arid Australia.

Associated with the measurement electrodes are solutions required for calibration, reference and storage (Fig. 1d). The Eh electrode will require a check solution such as Zobell's or Quinhydrone to standardise against the theoretical hydrogen electrode. Conductivity meters also have standard solutions based on type and range of measurements for calibration. Finally, saturated KCl is often used to store the probes in, but this may vary based on the type of electrode.

Other chemicals required are a high purity concentrated (69%) nitric acid for preservation of the cations sample and DI water (Fig. 1d). Acid is required (for one subsample) to ensure metals and metalloids remain in solution. This is particularly important for Fe^{2+} that may precipitate in the surface, oxygen-rich environment as Fe^{3+} oxyhydroxides, and in doing so adsorb other dissolved constituents biasing the results. Addition of acid can be done later in the laboratory to reduce potential for contamination. Samples should be kept cool and out of direct sunlight. We have not observed any problems from samples that were stored between 4°C and 35°C for periods less than two weeks.

Carbon sachets

Carbon sachets weighing approximately $1\ \text{g}$ (Fig. 1b inset) have been used in Australia to adsorb and concentrate certain metals from the water resulting in the low level (ng/L) detection of Au and PGE (Giblin 2001; Gray & Noble 2006). Direct analysis (Leybourne & Cameron *in press*) can be used with other fresh water samples, but the detection limits required are not consistently achieved in Australian saline samples. These sachets are presently manufactured by CSIRO (construction details are available from the authors). Exchange resins have been tested, but have not been used as extensively or as successfully as the carbon sachets (Gray & Noble 2006). A case study using the carbon sachets is presented in Noble *et al.* (this issue).

Generalized Sampling Method and Analysis

Not all sites are suitable for groundwater sampling. Site investigation is the first critical step to obtaining acceptable samples. Record notes on location, type of sample, type of casing (PVC or metal, open or closed, slotted) and potential contaminants, i.e. Fe from rusted pipe casing, excessive organics, drilling grease or dead animals in the water. It is important to note this or even exclude contaminated samples. A flow chart of the following sampling method is depicted in Figure 2.

Calibrate instruments

Calibration of instruments should be performed daily and checked if conditions change or irregular measurements are shown. The electrodes and meters should be checked against their required reference standards. Ensure the correct storage solutions for each electrode is used for probe longevity and accurate measurements.

Rinse equipment and set up filtration unit

The bailer or other water collection device should be rinsed with DI water prior to collection of each sample. Filtration equipment should also be thoroughly rinsed.

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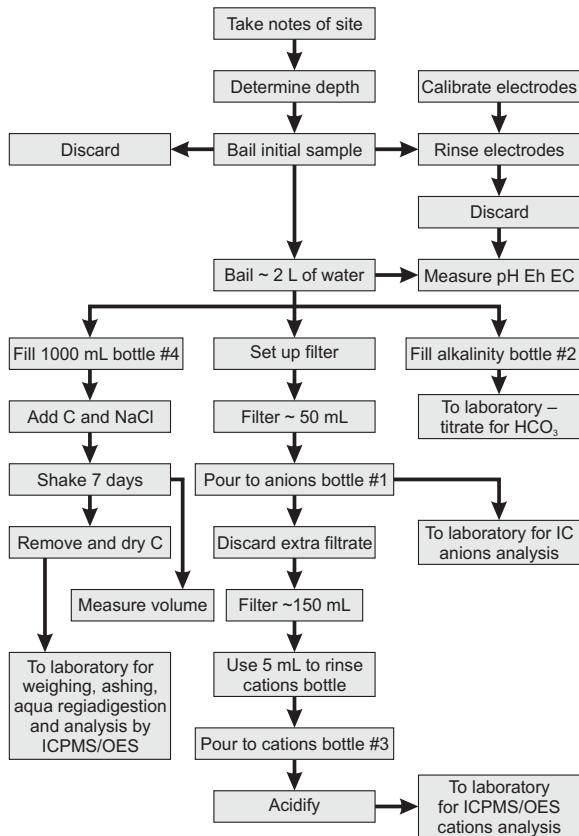


Figure 2. Flow chart of general method for hydrogeochemical sampling in Western Australia.

Place a new filter paper or syringe filter for each sample, being careful not to introduce dirt or contamination into the unit. Use a vacuum pump or syringe to filter the solution. Commonly, a two-person team should be used for groundwater sampling, with one person collecting the water and the other performing the “clean” work of the filtration, sample preparation and measurements.

Label bottles

A complete set of chemical analysis will require four bottles (isotope work is more specialized and not considered here). The bottles should be labelled with an identification number and the type of future analysis on the cap, shoulder of the bottle and main body of bottle.

- Bottle 1 will be used for anion analysis (125 mL bottle filled with ~ 50 mL)
- Bottle 2 will be used for alkalinity (125 mL bottle completely filled)
- Bottle 3 will be used for cation analysis (125 mL bottle filled with 125 mL)
- Bottle 4 will be used for carbon Au/PGE analysis (1 L bottle filled with ~1 L)

Sample groundwater

A bailer is lowered down a hole until the sampler hears or feels (the fall rate will slow) the top of the water. The depth to the water table should be recorded. This

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measurement can be completed separately and more accurately with the depth probe. Lower the bailer to the desired sampling depth or until refusal (bottom of hole) and retrieve the water sample. Consistency is the key to representative sampling, previous research by others has sampled, where possible, at least 5 m below the water table to avoid the chemical oxidation changes which occur close to the surface (Gray & Noble 2006; Giblin 2001 Appendix 2). The first water collected is a rinse for the bailer and also used to rinse the measurement electrodes. Repeat the bailing procedure until approximately 2 L of water is collected (excluding the first rinsed sample).

Groundwater measurement

Place the initial bailer rinse-water in a container with the electrodes on and start the devices, but do not record numbers. Tip the remaining water out of bailer. The second sample of water is used in the container to measure water parameters (tip out initial rinse). Record Eh, pH and EC over 5-15 minutes until stabilized. In some cases Eh may still vary up to 50 mV. Ideally, Eh measurements should be made in a flow-through cell to avoid the introduction of air into the sample that can cause erroneous measurements. For exploration purposes this is not often practical, but it is important to measure the water quickly after it is retrieved and not let to stand for more than 15 minutes. Reduced groundwater (measured < 200 mV) readings may decrease and then begin to rise. The minimum value is the most important for later data processing with this type of sample. A comparison of bailed versus pumped groundwater and the Eh differences are reported in Leybourne & Cameron (*in press*). For EC, pH (and Eh in most samples) the stable measurements are used. It is good practice to record all measurements over time.

Filtered samples

Initially filter approximately 50 mL of water. After all the water has passed through the filter membrane, pour the filtrate into the 125 mL bottle (bottle #1) for anions analysis. This sample is filtered, but not acidified. Pour another 150 mL of water into the top of the filter unit and filter. Pour approximately 5 mL into the bottle for cations analysis, cap and shake vigorously for 10 seconds. Discard this water. Finally fill the cations analysis sample bottle (bottle #3) with the remaining filtered water. This sample is acidified later with high purity nitric acid to 0.2% v/v or greater to ensure there are no Fe precipitates. Greater concentrations of acid can be used if precipitates remain after the initial aliquot of acid is added. Continue to add acid incrementally every few days until the Fe is dissolved.

The sample that is not acidified (bottle #1) is analysed for major anions by Ion Chromatography (IC) and independently for dissolved organic C and PO₄. The acidified sample (bottle #3) is analysed for major, minor and trace metals using by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and ICP-Optical Emission Spectrometry (ICP-OES) for the full suite of elements available.

Table 3. Elements/compounds with general detection limits and the analytical instrument or method used for Western Australian groundwater analyses. The elements Dy, Er, Eu, Gd, Hf, Ho, Lu, Nb, Pr, Sc, Sm, Ta, Tb, Th, Ti, Y, Yb and Zr are commonly below the detection limits by ICP-MS in this groundwater.

Element	Units	Method	Detection limits
Ag	ng/L	ICP-MS Carbon	5
Al	mg/L	ICP-OES	0.002
As	µg/L	ICP-MS	0.01
Au	ng/L	ICP-MS Carbon	0.5
B	mg/L	ICP-OES	0.1
Ba	µg/L	ICP-MS	0.01
Bi	ng/L	ICP-MS Carbon	0.5
Br	mg/L	IC	0.1
Ca	mg/L	ICP-OES	0.1
Cd	µg/L	ICP-MS	0.01
Ce	µg/L	ICP-MS	0.01
Cl	mg/L	IC	10
Co	µg/L	ICP-MS	0.01
Cr	µg/L	ICP-MS	0.01
Cu	µg/L	ICP-MS	0.01
DOC	mg/L	DOC analyser	0.2
F	mg/L	IC	0.01
Fe	mg/L	ICP-OES	0.004
Ga	µg/L	ICP-MS	0.01
HCO ₃	mg/L	Titration	1
K	mg/L	ICP-OES	0.08
La	µg/L	ICP-MS	0.01
Li	mg/L	ICP-OES	0.01
Mg	mg/L	ICP-OES	0.04
Mn	mg/L	ICP-OES	0.05
Mo	µg/L	ICP-MS	0.01
Na	mg/L	ICP-OES	0.006
Nd	µg/L	ICP-MS	0.01
Ni	µg/L	ICP-MS	0.01
NO ₃	mg/L	IC	1
Pb	µg/L	ICP-MS	0.01
Pd	ng/L	ICP-MS Carbon	3
PO ₄	mg/L	Titration	0.009
Pt	ng/L	ICP-MS Carbon	1
Rb	µg/L	ICP-MS	0.01
Sb	µg/L	ICP-MS	0.01
Si	mg/L	ICP-OES	0.5
Sn	µg/L	ICP-MS	0.01
SO ₄	mg/L	IC	3.5
Sr	mg/L	ICP-OES	0.008
U	µg/L	ICP-MS	0.01
V	µg/L	ICP-MS	0.01
W	µg/L	ICP-MS	0.01
Zn	µg/L	ICP-MS	0.01

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Detection limits vary depending on salinity levels, with more saline samples having higher detection limits due to increased dilution requirements. Many of the rare earth elements (REE), Au and PGE are below detection in groundwater samples from Western Australia, hence the use of the activated carbon sachet to concentrate Au and PGE to enable detection of these elements. Table 3 shows the full suite of elements, analytical instrument and achieved detection limits used by CSIRO for arid and semi-arid Australian groundwater. In other regions of Australia and the world the groundwater is fresher, requiring little or no dilution for analysis. In these environments much lower detection limits are achieved (0.1-1 ng/L) without the use of carbon for concentration.

Unfiltered samples

A 125 mL bottle (bottle #2) for alkalinity analysis is filled with sample water, making sure to exclude all bubbles and leaving no air space at the top. The 1000 mL bottle (bottle #4) for Au and PGE analysis is filled with unfiltered water to within 2 cm of the top. Using plastic tweezers, a carbon sachet is added to this bottle along with 10 g NaCl. This method varies from that reported in Giblin (2001) as her use of cyanide powder in the field was considered to be

too hazardous for general use.

The alkalinity sample is titrated with a known concentration of acid (e.g. 0.01M HCl) to an endpoint at pH = 4.3. Commercial laboratories can conduct this analysis, but it can also be performed in the field with a burette, stirrer and pH meter. A field alkalinity titration is a time consuming step in the field, making it less practical, and is often better done as soon as possible in a laboratory setting. Detection limits for the titration are approximately 5 mg/L.

The carbon sachet analysis is carried out at a commercial laboratory (presently Ultra Trace Ltd laboratories in Canning Vale, Western Australia). Sachets should be left in the sample bottle for at least 4 days and preferably placed on a bottle roller or shaker. The sachet is weighed (dry; 3 decimal places) and then the metals are determined by ashing, dissolution in aqua-regia and measurement using ICP-MS. The element suite is Au (0.1 µg/L), Pt (1 µg/L), Pd (1 µg/L), Ag (5 µg/L), with the reported lower detection limits in brackets. Using the sample weight and solution volume the final calculated values are an order of magnitude lower (ng/L). The analytical method described above has been previously tested for Au and PGE recovery in varying salinities, with activated carbon, with a recovery of ~95% (unpublished data). Field and analytical blanks, as well as

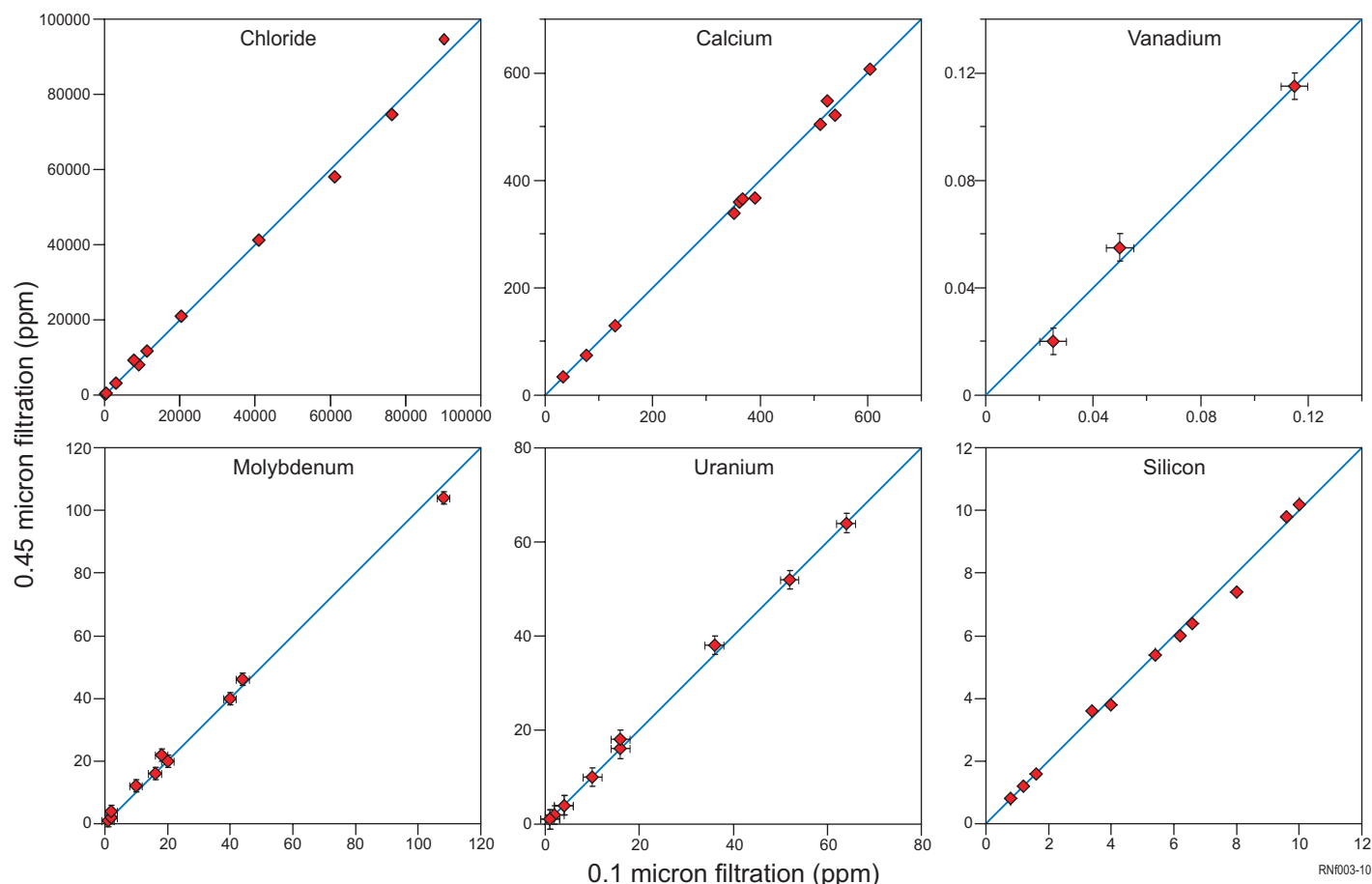


Figure 3. Chloride, Ca, Mo, U, Si and V concentrations compared from the 0.1 and 0.45 µm filtration treatment methods. The blue line represents a 1:1 correlation and with no differences between pore size. Error bars are applied based on the detection limit of the analysis (Gray & Noble 2006).

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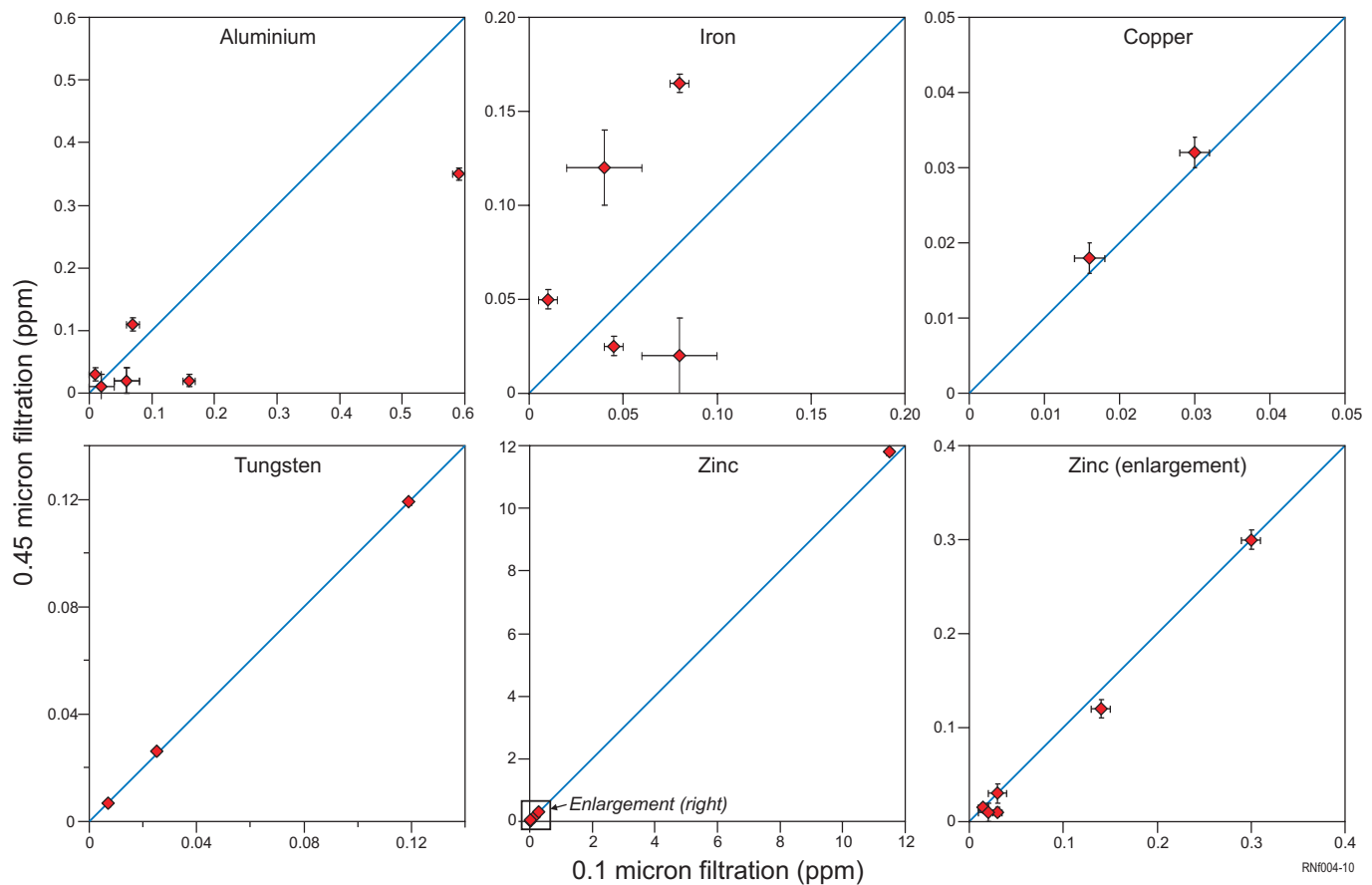


Figure 4. Aluminium, Fe, Cu, W and Zn (two difference scaled plots) concentrations compared from the 0.1 and 0.45 μm filtration treatment methods. The blue line represents a 1:1 correlation with no differences between pore size. Error bars are applied based on the detection limit of the analysis. Results were excluded where the concentrations were at or below the lower detection limit (Gray & Noble 2006).

field duplicates are used in all analyses for quality control.

Filter size comparison

A key consideration for the previously described sampling methods is influence of pore size in filtration. Studies by Hall *et al.* (1996) and Kennedy *et al.* (1974) have investigated the influence from filter pore sizes, but the samples tested were not from groundwater collected using the previously described methods. Clay minerals are commonly much smaller than 0.45 μm and theoretically could pass through a 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 pore size filters was conducted on 18 groundwater samples from a fresh to saline environment in the central Yilgarn and 11 fresh groundwaters from the NE Yilgarn Craton. Both gave similar results, with the later test described in detail below.

The results for U, Mo, Si and S show no difference between the two pore sizes (Figs. 3 & 4), similarly to the patterns for major anions and cations (Fig. 3). Vanadium,

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W and Cu and to a lesser extent Ni (not shown) and Zn also indicate no difference (Fig. 4), but there are fewer samples for comparison as many samples were below detectable concentrations. Greater salinity increases the required dilution and in turn increases the detection limits. However, Al and Fe show significant, random variability. Aluminium concentrations are higher in the 0.1 μm pore size filter samples as compared to 0.45 μm pore size filter. This higher concentration for the finer pore size does not support the idea that small clay minerals (aluminosilicates) are passing through the 0.45 μm filter and being retained by the 0.1 μm filter. In comparison, the near-perfect correlation between filter sizes for Si suggests the greater dissolved Si concentrations are not influenced by the comparatively smaller 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 they are not influenced by Al and Fe colloids i.e. Al and Fe do not irreversibly adsorb the dissolved trace metals. Based on these data, Gray & Noble (2006) concluded the use of either tested filter pore size is acceptable for groundwater exploration in the NE Yilgarn. The more widely available, faster filtering and less expensive 0.45 μm pore size is preferred.

CONCLUSIONS

Groundwater sampling methods are easy to use and are accessible to most industry explorers (with limited hydrogeochemical background) to develop a successful groundwater exploration program with the general procedure of this paper and associated literature references. This method is most useful in the arid and semi-arid regions of Western Australia where access can be difficult and the groundwater is highly variable in pH, salinity and depth (from the surface).

Tests have shown the 0.45 μm pore size filters were cost effective and of sufficiently small pore size for groundwater sample preparation. Activated carbon sachets added to 1000 mL of unfiltered groundwater can be routinely used for Au and PGE analysis, successfully lowering detection limits by up to three orders of magnitude in saline groundwater. Improving detection for elements in saline samples will enhance the chances for exploration success in the future.

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Ryan R.P. Noble and David J. Gray
CSIRO Earth Science and Resource Engineering
Minerals Down Under Flagship
 PO Box 1130
 Bentley, 6102 Australia
 Email: ryan.noble@csiro.au

