



**ALS Methods**  
**ME-MS14L™**  
**MS14L-ANPH™**  
**MS14L-REE™**  
**MS14L-PbIS™**

# Hydro-geochemistry for Exploration

## Why Hydrogeochemistry?

The direct detection of buried mineral deposits is a major challenge for the exploration industry. Exploration through cover has traditionally used drilling to sample the top of the units of interest and/or geophysical methods. For deposit types that don't have well-defined geophysical signatures and regions too large to make close spaced grid drilling possible there have been limited exploration tools.

Continuing advances in ICP-MS technology have pushed detection levels into the ppb range for large suites of elements allowing the sampling of non-traditional media such as plant material, water and the surfaces of grains. Hydrogeochemical sampling of water to identify the composition of the rocks that it has interacted with can help explorers to identify buried mineralization.

Water that has interacted with mineralization will take on elements from the ore which are then transported with the water producing larger footprints than most solid media samples. Biogeochemistry will have a similar sized footprint; however, in areas without consistent coverage of a single species the application of this method is not



possible. Hydrogeochemistry has the potential to open large regions with substantial transported cover by allowing broad spaced sampling, of a similar scale to stream sediments, to narrow down prospective areas to a size where grid drilling is feasible.

A major advantage of Hydrogeochemistry is that sample collection from existing water sources (surface and existing wells) is non-invasive. For early stage exploration it may be the only type of sample that can be taken from an area before extensive permitting is obtained.

Improvements in ICP-MS technology have brought detection limits to within an order of magnitude of those produced by high resolution HR-ICP-MS instruments. An advantage to using traditional ICP-MS instrumentation for hydrogeochemistry is that they can accommodate higher total dissolved solids in samples reducing the need for sample dilution.



## At what stage of exploration?

Hydrogeochemistry is an effective tool at the greenfields stage of exploration where large regions of ground need to be evaluated using sparsely spaced samples. It also has the potential to be used for targeting at the brownfields stage where characteristic element associations can be identified in water that has interacted with the sought mineralization style. Sampling from drill holes can be useful to identify where drill holes have come close to mineralization but not intersected it, as a chemical signature may be seen in waters without corresponding mineralization or alteration in the rocks. This is particularly useful when exploring for mineralization styles that don't have a large visible alteration footprint which make near misses difficult to identify.

Another advantage of collecting hydrogeochemical samples at the exploration stage of a project is to have a base line water geochemistry dataset. If the project proceeds to mining this information can be useful for environmental planning and can provide a helpful baseline water quality assessment. Even without the project progressing to mining, Hydrogeochemistry can provide valuable information about water quality of a region and form part of a company's community social responsibility when supplied to local authorities. Many of the variables measured for mineral exploration are also important for determining the quality of water for human and agricultural use.

## Collecting Samples

Due to the very low-levels of detection used in Hydrogeochemistry, contamination can be a potential concern. To remove the chance of contamination in the sampling process a rigorous cleaning routine is recommended. Bottles should be rinsed a minimum of 3 times with sample water before the final sample is collected, and all metallic jewelry should be removed at least one day before sampling to allow any metal transferred onto skin to wear off. To monitor the sampling protocol a high rate of QA/QC sampling is recommended. This ideally would consist of duplicates, blanks (deionized water) and reference waters.

During field collection it is essential to record physical parameters of the water sample at the time it is removed from the source. Readings ideally would



include the temperature, Eh (ORP), TDS, Conductivity and pH. The temperature, Eh and pH of samples will change after collection, so these parameters are best collected at the time of sampling rather than later at the laboratory stage. These physical parameters will be essential for the interpretation of analytical results and some can be used as exploration vectors themselves (pH and Eh).



## Sample Preparation and Analyses

A minimum of two separate filtered samples are needed for full hydrogeochemical analyses. The concentration of metals and pathfinder elements are determined by ME-MS14L™ and analyses of anion species (Br, Cl, F, NO<sub>2</sub> and SO<sub>4</sub>) and alkalinity is by MS14L-ANPH™. Any add-on analyses will use the remaining sample prepared for the ME-MS14L™ and MS14L-ANPH™ methods.

The sample prepared for ME-MS14L™ should be filtered at 0.45µm and acidified with ultra-pure nitric acid to lower the pH to approximately 2. The acidification will maintain dissolved metals in solution and the removal of particles will ensure that only dissolved species are measured during analyses. The sample collected for anion and alkalinity measurement should also be filtered at 0.45µm and the bottle filled to a positive meniscus to prevent air interacting with the sample. The anion-alkalinity sample should not be acidified.

ME-MS14L™ ANALYTES & DETECTION LIMITS (µg/L)							
Au	0.002	Cu	0.1	Ni	0.2	Ta	0.01
Ag	0.005	Fe	0.003mg/L	P	0.005mg/L	Te	0.01
Al	3	Ga	0.05	Pb	0.05	Th	0.005
As	0.05	Hf	0.005	Pd	0.005	Ti	0.2
B	3	Hg	0.05	Pt	0.005	Tl	0.002
Ba	0.05	In	0.01	Rb	0.01	U	0.002
Be	0.005	K	0.01mg/L	Re	0.002	V	0.05
Bi	0.01	La	0.005	S	0.2mg/L	W	0.01
Ca	0.02mg/L	Li	0.1	Sb	0.01	Y	0.005
Cd	0.005	Mg	0.005mg/L	Sc	0.01	Zn	0.5
Ce	0.005	Mn	0.05	Se	0.05	Zr	0.02
Co	0.005	Mo	0.05	Si	0.03mg/L		
Cr	0.5	Na	0.01mg/L	Sn	0.05		
Cs	0.005	Nb	0.005	Sr	0.05		

MS14L-REE™ ANALYTES & DETECTION LIMITS (µg/L)							
Dy	0.005	Gd	0.005	Nd	0.005	Tb	0.005
Er	0.005	Ho	0.005	Pr	0.005	Tm	0.005
Eu	0.005	Lu	0.005	Sm	0.005	Yb	0.005

MS14L-ANPH™ ANALYTES & DETECTION LIMITS (µg/L)							
Br	0.05mg/L	NO <sub>3</sub>	0.005mg/L	pH	0.1 units	Cond.	2µS/cm
Cl	0.5mg/L	SO <sub>4</sub>	0.5mg/L	TDS	3mg/L	Alkalinity	1mg/L
F	0.02mg/L						

## Interpreting Results

As mentioned earlier, field readings of physical parameters of hydrogeochemical samples are essential to enable interpretation of analytical results. An example of this is the variable element carrying capacity of acid-oxidizing compared neutral-reducing waters.



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One element that shows large variation between acid-oxidizing waters and neutral-reducing waters is Mo. As Mo is more soluble in a neutral-reducing water the background concentrations will be higher than those in a water that is acidic and oxidizing where Mo had limited solubility. The relationship is the opposite for metals transported as cations such as Cu. These elements are much more soluble and easily transported in waters that are acidic compared to water that is neutral to alkaline. Understanding these different element behaviors is an essential part of the interpretation of hydrogeochemistry and knowing your water pH-Eh ranges is vital.

Another parameter that affects the concentration of elements in a sample is the salinity of the water. Highly saline water has a higher carrying capacity for metals, therefore background in a salty water will be much higher than background in a low salinity water. If the different water characteristics are identified using field readings the level of what constitutes an anomalous concentration can be more easily quantified.

As water is mobile the footprint of anomalies can be used to vector back to mineralization if the water flow direction is known. So, a hydrological understanding of the area of exploration is also an important step for using hydrogeochemistry for targeting.

A useful reference for a description of hydrogeochemical sampling methodology is: Gray, D., Noble, R., and Gill, A., 2011. Field guide for mineral exploration using hydrogeochemical analysis. CSIRO Earth Science and Resource Engineering.

If you think Hydrogeochemistry may be the right tool for your project and you would like to add it to your current exploration methods, please feel free to contact us for assistance in setting up your sampling kit and procedures.

ALS METHOD CODE	DESCRIPTION
ME-MS14L™	Super Trace Analysis of water samples analyzed directly by ICP-MS & ICP-AES. Ideal for ground and surface waters.
MS14L-ANPH™	Anions (Br, Cl, F, NO <sub>2</sub> , SO <sub>4</sub> ) by ion chromatography and a full suite of physical parameters (pH, TDS, Conductivity, Alkalinity).
MS14L-REET™	Add on to the ME-MS14L™ method. Rare Earth Analytes are reported to trace detection limits by ICP-MS.
MS14L-PbIS™	Add on to the ME-MS14L™ method. Lead Isotopes are reported to trace detection limits by ICP-MS.
Isotopes: S, C, O, H, Cu	Analyses of these isotopes can be facilitated with Queens University.

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