

WEAK VS. STRONG LEACHANTS

INTRODUCTION

One of the most common ways to obtain a reading of the concentrations of elements in a soil (or rock) is to carry out a wet chemical digestion. Elements in the resulting solution are then passed through an instrument, the concentration in the solution recorded and the concentration in the original solid is back calculated. It is usually the case with most solids that not all of the solid material is dissolved, even in an aqua regia or four acid digest some material usually remains. All wet chemistry to some extent is a partial digestion. The question is to what degree. The diagram below shows a number of different digestion/extraction (leachant) types arranged in order from strong to weak.

PROPERTIES OF DIGESTING/ EXTRACTING SOLUTIONS

Historically, when analysis instruments and instrument detection limits were inferior, it was a desirable feature that the leachant dissolved as much of the solid matrix as possible in order to maximize the concentration of available analytes. With modern instrumentation such as the Inductively Coupled Mass Spectrometer (ICPMS), obtaining detectable amounts of most elements from most soils is no longer a major issue. Strong digestion solutions have a number of undesirable features. Firstly, in a strong digest, high concentrations of "matrix" elements such as silica, iron and calcium are taken into solution; these can cause interference effects when low concentrations of other analytes are being sought. Secondly, it is now realized, that weaker leachants provide better signal to noise resolution. In a recent CAMIRO study (Hamilton et al, 2001) Pb isotope work showed that a weak digestion contained Pb isotopes more closely related to the Pb isotopes in the mineralization source at depth, than did the Pb (isotopes) contained in a stronger digest. The latter contained a more "mixed" signal which included a great deal of "background" Pb from other sources. Choosing the best extraction solution to "vector to ore" is more complicated than simply choosing the solution which provides highest concentrations of analytes. Clearly a compromise is required – an extraction of sufficient strength to extract and retain the elements of interest during analysis, but not so strong that

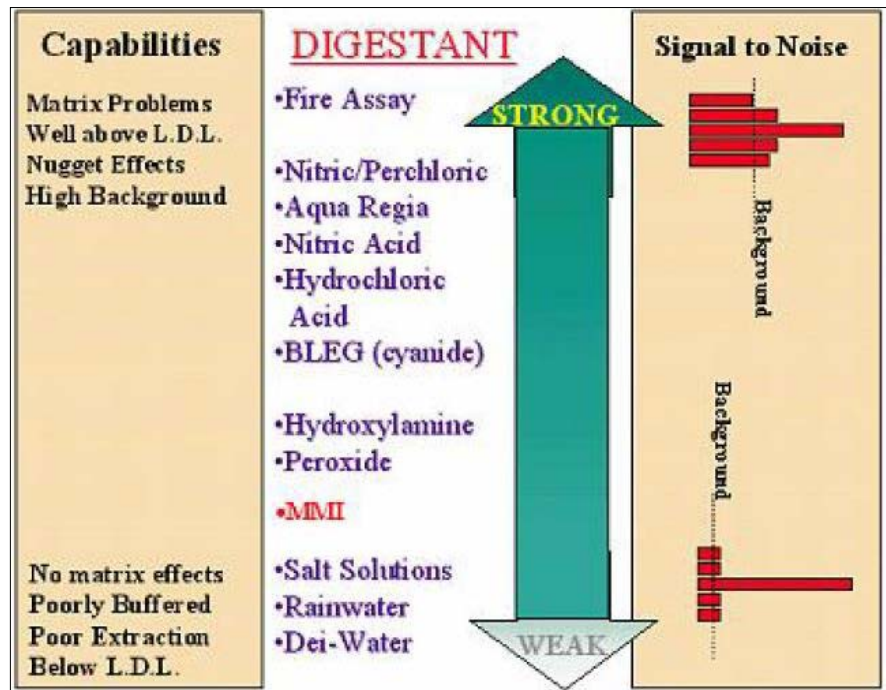


Figure 1: Properties of Different Strength Digestions

matrix and background effects become an issue. That is why partial digestion/ extraction of soil samples is now a very commonly used procedure.

In Figure 2, a number of different partial extractions and digestions are listed.

Firstly, note the distinction made between a partial digestion and a partial extraction. A partial digestion attempts to preferentially dissolve in its entirety, one or more phases of a soil. This may be the organic matter, iron oxides, manganese oxide or carbonate. Analytes associated with the selected phase are then taken

into solution as well. If only one phase is dissolved the digestion is selective, if a number of phases are dissolved it is non-selective. On the other hand, an extraction attempts to remove from the exterior of the soil particles, any attached analytes. Some extractants are believed to selectively remove adsorbed analytes from a single phase; others, the non-selective

extractants extract adsorbed analytes from a number of phases.

Some of the latter, including MMI™, dissolve the adsorbed analytes by complexing with them. The MMI™ extractant solutions contain a number of strong ligands. A ligand is simply an inorganic or organic ion which forms a strong bonding complex with the element of interest. A ligand makes it more energetically favourable for the analyte to be in solution rather than adsorbed to the outer surfaces of the soil particles. It has the added advantage that it remains complexed with it, keeping it in solution (and preventing re-adsorption) during the analytical process – that is, up until the stage of plasma excitation. Collectively digestion and extraction solutions are sometimes called leachants.

Relative Performance of Weak and Strong Leachants

One of the most convincing (and independent) comparative surveys to show the relative merits of weak versus strong leachants of a soil took place at Cross Lake in the Abitibi belt of Canada during the CAMIRO study in 1999 and 2000. Cross Lake is a small VMS type deposit, beneath 30-35m of glacial overburden (clay, till, sand), approximately 8,000 years old. A number of digestion solutions and extractants of different strengths were used on soil samples taken from shallow soils across the deposit. The results are shown in Figure 3.

Figure 3. Analytical results from different strength digestion and extraction solutions, Line 40W Cross Lake, 1999. Zn values in aqua regia (AR), Enzyme Leach (EL), MMI™ (MMI™) and water (W). (After Hamilton et al., 2001) The location of the mineralized zone 35m beneath the surface is shown as the black bar near the centre top of the diagram. Of the five solutions trialled, which included water as a very weak extractant, and aqua regia as the strongest digestant, MMI™ shows the greatest signal to background contrast. It is of note that whilst the aqua regia digest results in a higher concentration of Zn in solution (ppm range) the signal to noise ratio, and anomaly definition is very poor. The exercise was repeated on an adjacent line. Results are shown in Figure 4.

Figure 4. Analytical results from different strength digestion and extraction solutions,

	SELECTIVE	NON-SELECTIVE
DIGESTIONS	Ammon. Oxalate (am. FeOx)	Dil nitric
	Hydroxylamine (Mn+Feox)	Dil hydrochloric
	Hydrogen Peroxide (MnOx)	Sodium Hydroxide
	Enzyme Leach (MnOx)	Aqua Regia
	NaOCl(organics)	
	Acid-acetate (carbonates)	
EXTRACTION	EDTA (am. FeOx)	Magnesium Chloride
	Sod. Pyrophosphate (Organics)	Ammon. Acetate
		BLEG
		MMI-A, B & M

Figure 2: Partial Digestion and Extraction Solutions

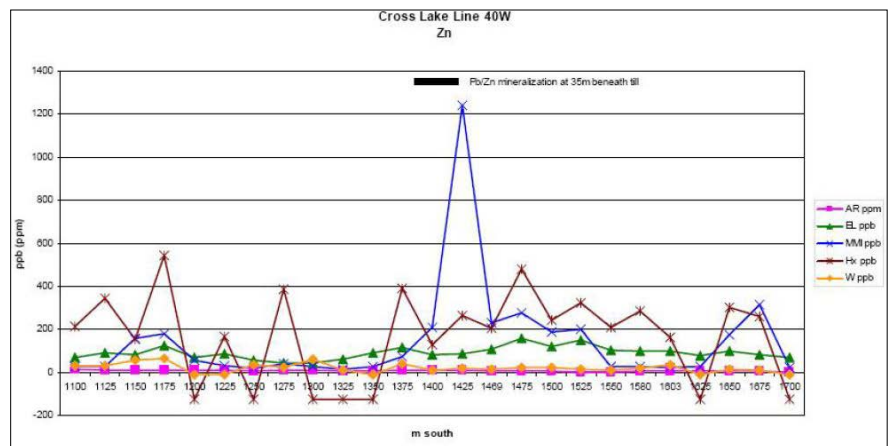


Figure 3: Analytical Results from Different Strength Digestion and Extraction Solutions, Line 40W Cross Lake, 1999. Zn Values in Aqua Regia (AR), Enzyme Leach (EL), MMI™ (MMI™) and Water (W). (After Hamilton et al., 2001)

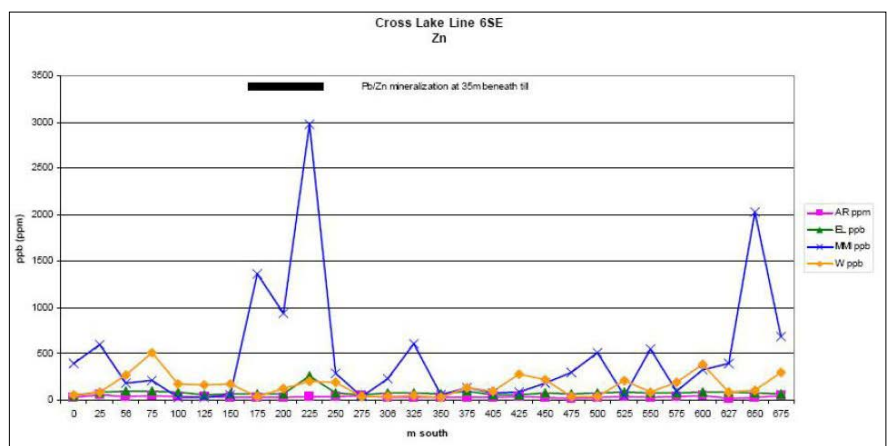


Figure 4: Analytical Results from Different Strength Digestion and Extraction Solutions, Line 6SE Cross Lake, 1999. Zn Values in Aqua Regia (AR), Enzyme Leach (EL), MMI™ (MMI™) and Water (W). (Hamilton et al. 2001)

Line 6SE Cross Lake, 1999. Zn values in aqua regia (AR), Enzyme Leach (EL), MMI™ (MMI™) and water (W). (Hamilton et al. 2001) Initially it was thought that the depth of sampling may have played a role – MMI™ was sampled routinely 10-25cm below the soil interface, whereas other techniques sampled the B horizon which had varying depths. However, examination of the depth profiles (Figure 5 & 6) shows this not to be the case.

The diagram above shows that at over 50% of the sites the depth of sampling was very similar – the B horizon was 10-25cm below the sample interface. Of particular importance, where the crucial anomalous sample was taken (1425S) the depths sampled were identical.

Figure 6 shows this also to be the case on the second line (6SE) sampled.

In the year 2000 the entire exercise was repeated, with all samples being sampled at a depth of 10-25cm. Whilst slightly improved responses were obtained for the Enzyme Leach and another weak leach, MMI™ gave the same very high contrast. Clearly there is a reason for this; the ligands selected for MMI™ extraction provide the optimum compromise in leachant strength, whilst not attacking the soil matrix.

DISCUSSION AND CONCLUSIONS

The accepted labels “weak” and “strong” leachant, are based on ability to attack substrate. As it transpires, MMI™, the optimum leachant in the case above is in fact a strong extractant for the metals, and weak only in its (required and deliberate) ability to not attack the substrate. These results suggest that a greater proportion of the Zn directly attributable to the deposit resides in an adsorbed form which has been made soluble by the strong ligand. Conversely much of the background Zn which is less directly linked to mineralization, and which has been re-worked by mechanical processes over time, resides internally within soil phases and is only released by strong digestion solutions.

Figures 7(a) and 7(b) show schematically how an MMI™ extraction solution achieves the dissolution of adsorbed copper ions.

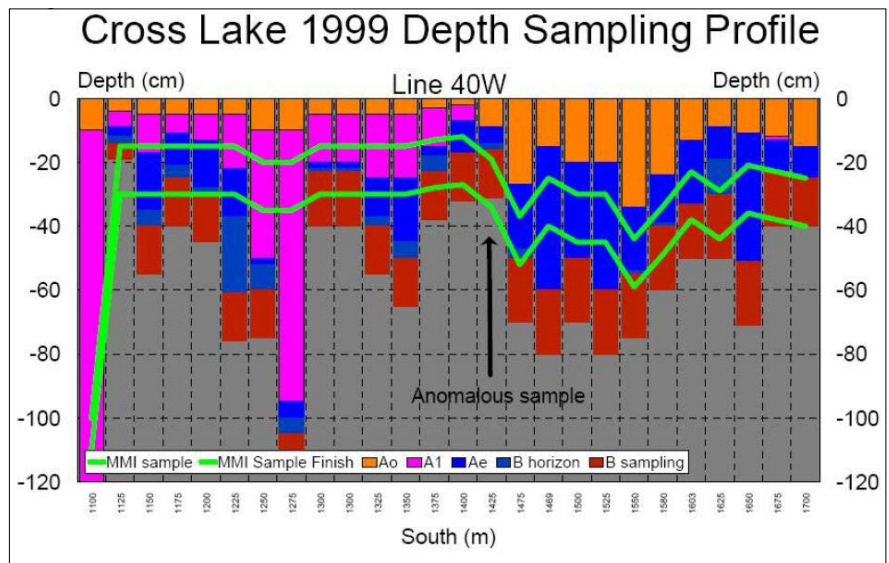


Figure 5: Depth of Sampling, 1999CAMIRO Survey, Line 40W Cross Lake

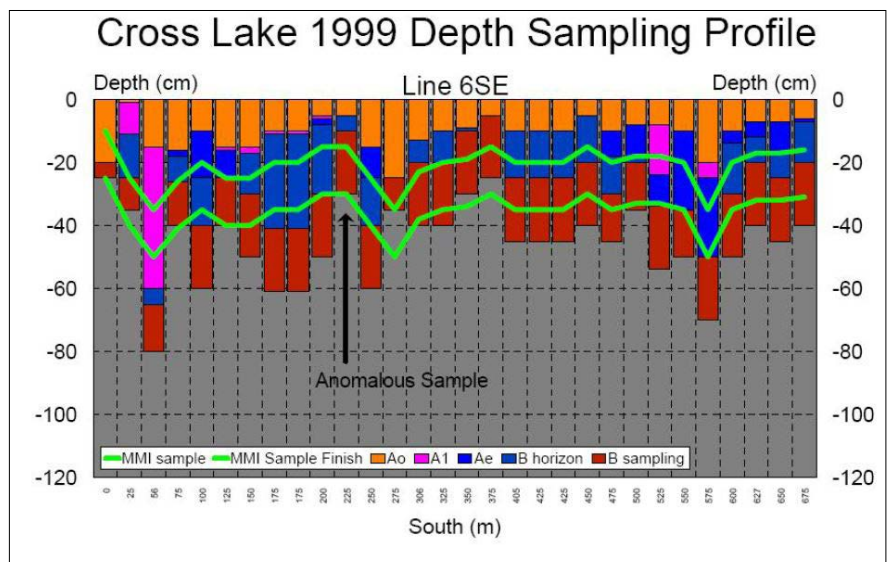


Figure 6: Depth of Sampling, Line 6SE, Cross Lake

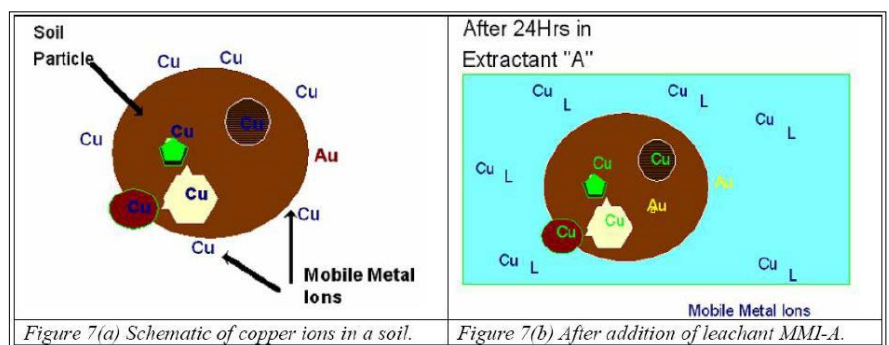


Figure 7: How an MMI™ Extraction Solution Achieves the Dissolution of Adsorbed Copper Ions.

Figures 8(a), (b) and (c) are part of a conceptual model (Mann et al, 1998) which explains in greater detail how this is believed to result in superior signal to noise ratio and sharper definition of anomalies. In Figure 8(a), the vertically ascended ions from an oxidizing ore deposit are shown.

After vertical ascension, the ions are lodged in the top 10-25cm of the soil layer as adsorbed ions, by the combined effects of capillary rise and evaporation. During soil forming processes (pedogenesis) the adsorbed ions are, over a geologically relatively short period of time, incorporated into soil particles as shown in Figure 8(b). At any one instant of time there will be both unbound (yet to be bound) and bound forms in the soil profile, the latter generally out-numbering the former. Mechanical dispersion processes (Figure 8(c)), again over relatively short periods of time cause metals to disperse. As unbound metals are relatively short-lived (an intermediate product) the net result is that only bound metals are found in the soil away from the point of initial emplacement in the soil. As a consequence, extraction procedures which target unbound (adsorbed) ions, give better definition (both amplitude and position-wise) of the initial point of emplacement in the soil, and consequently better target definition of the ore-body.

REFERENCES

- Hamilton, S.M., Cameron, E.M., McClenaghan, M.B., & Hall, G.E.M. 2001. Deep penetrating geochemistry – Cross Lake final report. In: Cameron, E.M. (ed.) Deep Penetrating geochemistry Phase II. CAMIRO.
- Mann, A.W., Birrell, R.D., Mann, A.T., Humphreys, D.B. and Perdix, J.L. (1998). Application of the mobile metal ion technique to routine geochemical exploration. J. Geochem. Explor., 61 (1-3), 87- 102.

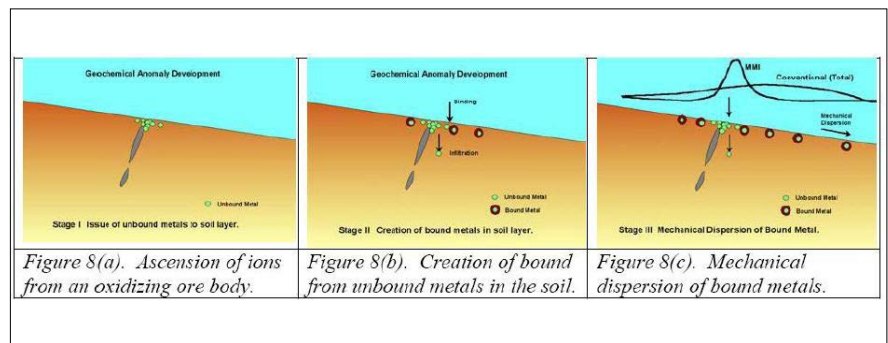


Figure 8: Conceptual Model

CONTACT INFORMATION

Email us at minerals@sgs.com
www.sgs.com/mining