

# The Evaluation of Geological Exploration Samples using Multi-element Mobile Metal Ion (MMI-M) Selective Weak Extraction and Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

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## ABSTRACT

*The multi-element determination of geological samples is of considerable importance in the evaluation of potential resources. Increases in the understanding of elemental behaviour, combined with the development of software for handling multi-element arrays, have led to the use of a large suite of elements as pathfinders for mineralization. Techniques such as inductively coupled plasma mass spectrometry (ICP-MS) have become synonymous with the analysis of the large volumes of samples for a wide range of elements required by geological surveys. The aim of this work was to explain how the design of the ICP-MS detector enables the measurement of both high and low concentrations of elements in a single analysis. This will be illustrated by the analysis of forty-five elements in a case study using the multi-element MMI-M selective weak leach technique.*

## INTRODUCTION

The determination of major, minor and trace elements in geological samples has always been of paramount importance in the geochemical exploration of elements of economic interest and the evaluation of potential resources. However, these types of samples pose an unusual set of challenges for the analyst, including: the range of analyte concentrations present; the number of elements required per sample; and the volume of samples produced by a typical exploration survey. These factors are further compounded by the presence of a complex range of matrices and the potential for widely different compositions within an analytical batch of samples (Riddle, 1993).

Over the past decade, inductively coupled plasma mass spectrometry (ICP-MS) has pushed the boundaries of both detection limits and the range of determinable elements available to the exploration geologist. An increasingly sophisticated understanding of elemental behaviour and the development of software for handling multi-element arrays, has gone hand in hand with the development of the multi-element capability of ICP-MS, leading to the use of a large suite of elements as pathfinders for mineralization. Like most commercial analytical laboratories, SGS Minerals Services has developed a comprehensive range of multi-element techniques depending upon the analytical and budgetary requirements of the client. Initial reconnaissance samples (or soil samples) generally require a partial or weak extraction – a hydrochloric/nitric acid

extraction or selective weak extraction (Mobile Metal Ion) – followed by an elemental scan to provide information concerning anomalies above background levels. Follow-up drilling, delineation, and rock samples are generally analysed using a multi-acid digestion to provide more complete information about composition.

Multi-element scans can thus provide a wealth of elemental data in rapid timeframes for the large volumes of samples required by exploration geochemistry. The aim of this work was to explain the principle behind ICP-MS and to show how developments in the design of the detector allow the technique to overcome its main limitation; the inability to measure high concentrations of elements. This will be illustrated by the analysis of both high and low concentration samples from a case study carried out at the Namex Explorations Inc. Huffman Lake Property (Ontario, Canada) using the MMI-M technique, highlighting the ability of ICP-MS to provide unparalleled analytical data for the geologist.

## Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS utilizes an argon plasma as an efficient heat source for the formation of positive ions. A small portion of the ions enters the instrument, is focused using a lens system, and then passes into a quadrupole mass spectrometer, where ions are separated based on their mass to charge ratio. An electron multiplier is used to detect the ions as they pass out of the mass spectrometer.

By comparing intensities from known standard solutions to the unknown sample, the concentration of the analyte can be determined.

The advantages of ICP-MS for geological analysis include:

- The sensitivity of the technique allows for the determination of many elements in the sub parts per million range (e.g. rare earth elements).
- The multi-element capability allow for the analysis of a wide range of elements at different concentration levels in one pass.
- The reliability of contemporary instrumentation makes it a powerful tool in the analysis of the large volumes of samples generated in geochemical analysis.

The main limitations of ICP-MS for geological samples are:

- It cannot directly determine elements in solutions containing high levels of dissolved solids, such as rock digests.
- The high temperature of the plasma can cause polyatomic interferences (such as argides and oxides of other elements in the sample digest).
- The high sensitivity of the instrument makes it inappropriate for high analyte concentrations.

Whilst the first two disadvantages can be overcome by diluting the sample prior to analysis, optimizing the sample introduction system to reduce polyatomic interferences, choosing the appropriate isotope and where necessary performing interference corrections, the measurement of increased ion beam intensities from high element concentrations requires a different approach; the dual stage detector.

#### Increased Dynamic Range for ICP-MS – The Dual Stage Detector

Commercially available ICP-MS instruments now contain a two-stage, or dual detector, for the measurement of low (sub parts per billion) and high (parts per million) solution concentrations in a single pass. High intensity ion signals emanating from the quadrupole mass spectrometer are measured by the analogue stage, whereas low concentrations pass into the electron multiplier for amplification and measurement – the pulse stage. It is this amplification that enables the ICP-MS to detect very low concentrations of elements in solution. By measuring solutions containing significant concentrations of an analyte using both stages of the detector, a cross calibration coefficient can be determined. This determination can be repeated for all elements of interest to create a dual detector calibration. Due to the linear nature of the detector, sample digests containing a wide range of concentrations can now be determined in a single pass, without the need for further dilution. For example, lead concentrations measured using a maximum calibration of 0.050mg/L have been shown to be linear from 0.0001mg/L up to 10mg/L, and elements such as magnesium, iron and aluminum can be measured quantitatively at levels of greater than 50mg/L in solution.

#### MOBILE METAL ION (MMI) ANALYSIS BY ICPMS

Partial weak extractions, such as Mobile Metal Ion Geochemistry (MMI), have become a significant tool in geochemical exploration over the past decade (Mann et. al., 1998). Earlier versions of these leaches measured four or five indicator elements at low concentrations using ICP-MS in order to determine locations of buried gold and base metal mineralization. The recent introduction of MMI-M, a pH neutral extraction that aids in the identification of polymetallic targets and multi-element associations for specific styles of mineralization, has placed the emphasis on ICP-MS to deliver quantitative results for a much larger range of elements. As well as measuring base and precious metals, MMI-M has been used in the determination of rare earth elements (significant in the lithochemistry of kimberlite and nickel sulphide deposits) and major elements such as Fe, Ca and Mg. In total, ICP-MS can be used to measure at least 45 elements (see Table 1) present in concentrations ranging from sub parts per billion (e.g. Au and Th), through to hundreds of parts per million (e.g. Mg and Ca), illustrating the major advantage of the dual detector approach to analysis by ICP-MS.

**Table 1: Element list and Detection Limits (D.L.) for the Multi-element MMI-M analysis. All detection limits in mg/kg.**

Element	D.L.	Element	D.L.	Element	D.L.
Ag	0.001	Fe	1	Sm	0.001
Al	1	Gd	0.001	Sn	0.001
As	0.01	La	0.001	Sr	0.01
Au	0.0001	Li	0.005	Ta	0.001
Ba	0.01	Mg	1	Tb	0.001
Bi	0.001	Mo	0.005	Te	0.01
Ca	10	Nb	0.0005	Th	0.0005
Cd	0.001	Nd	0.001	Ti	0.003
Ce	0.005	Ni	0.005	Tl	0.0005
Co	0.005	Pb	0.01	U	0.001
Cr	0.1	Pd	0.001	W	0.001
Cu	0.01	Pr	0.001	Y	0.005
Dy	0.001	Rb	0.005	Yb	0.001
Er	0.0005	Sb	0.001	Zn	0.02
Eu	0.0005	Sc	0.005	Zr	0.005

#### METHODS AND MATERIALS

50g of sample was shaken for 20min with 50mL of MMI-M Selective Weak Extraction Solution (Wamtech, Australia). The solution was allowed to stand overnight and analysed by ICPMS (Elan 9000, PerkinElmer/SCIEX, Concord, Canada). The instrument was calibrated using a blank, 0.010mg/L (0.001mg/L for Ag, Au, Pd and 1mg/L for Al, Ca, Fe, Mg) and 0.050mg/L (0.005µg/L for Ag, Au, Pd and 5mg/L for Al, Ca, Fe, Mg) standards, all containing the MMI-M matrix.

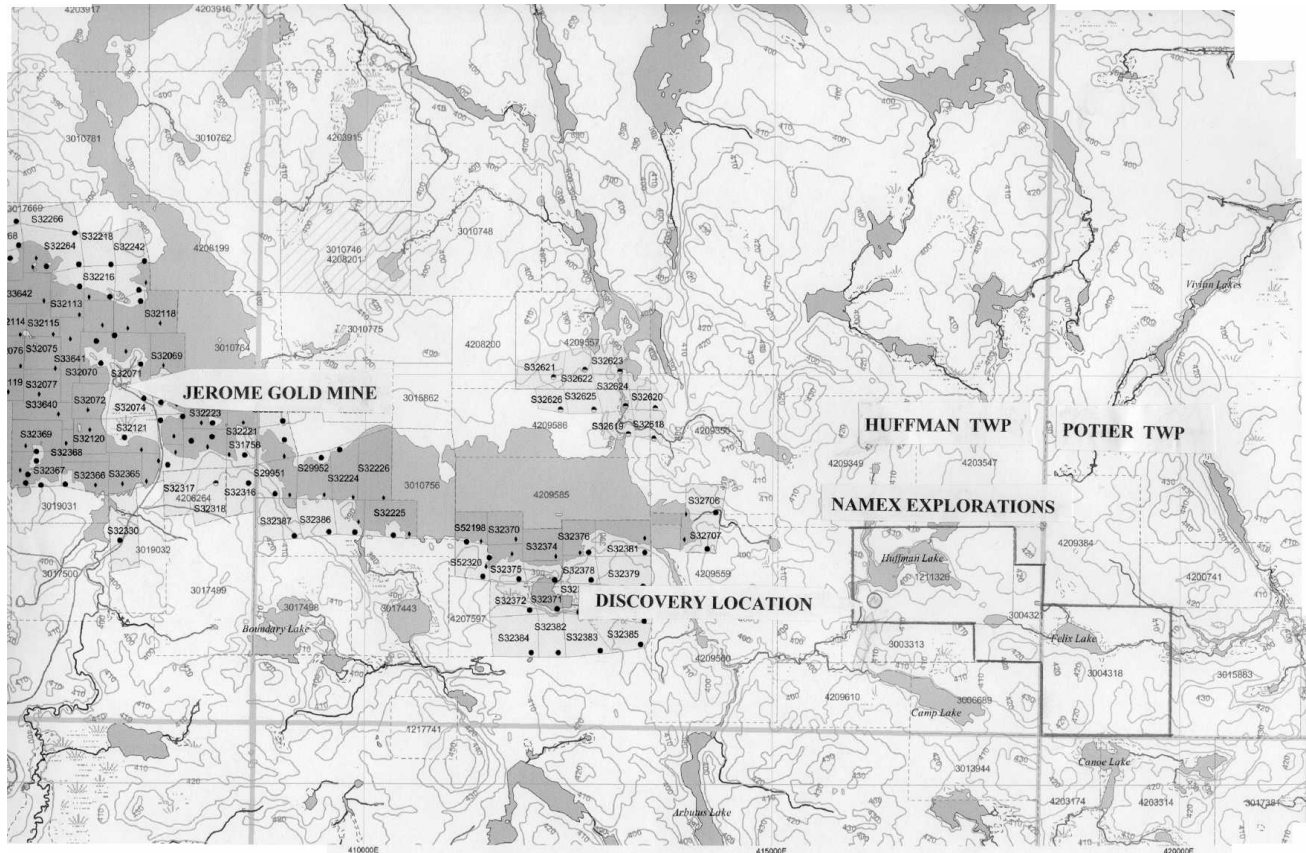


Figure 1: Location of the Huffman Lake Property, Ontario, Canada

## RESULTS

### MMI-M Survey Results from The Namex Huffman Gold Property

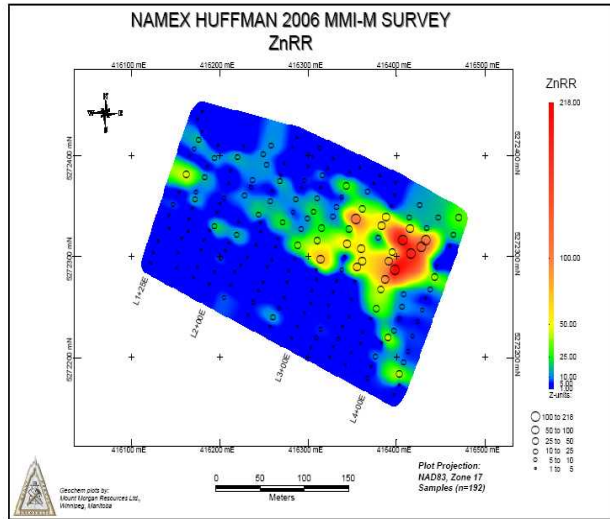
The Namex Huffman property, located 24 miles south of Timmins, Ontario, in the Swayze Gold Belt (Figure 1), was surveyed using the MMI-M technique. One hundred and ninety six samples were taken on a grid pattern and analysed using the MMI-M selective weak extraction with ICP-MS finish. Forty-five elements were measured in a single pass analysis, ranging in concentration from single parts per billion (0.001mg/kg) for elements such as gold and silver, up to several hundred mg/kg for major component elements such as aluminum, iron and calcium. Individual element responses were plotted using response ratios, from which the interpretation was based.

Response ratios were calculated for each element using the following procedure. The lowest quartile (25%) of the data for that element is selected, including results that are less than detection limit, by using a value of half the detection limit. The mean of the lowest quartile was determined and used as the background for that element. For each sample the element response was divided by the background value and rounded to whole numbers.

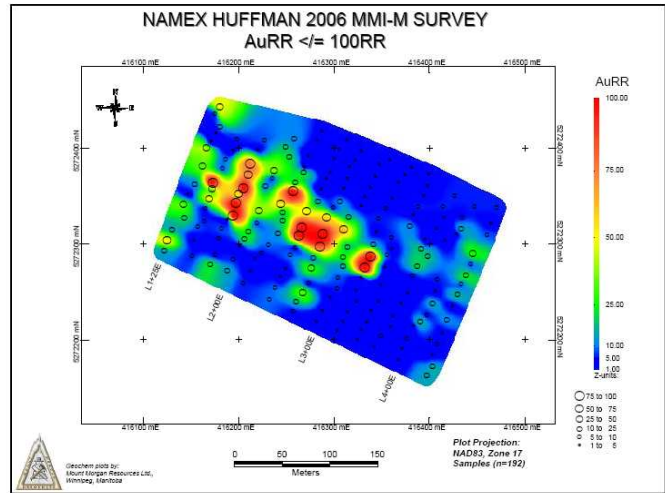
Examples of the response ratio lots from the MMI-M data are shown in Figures 2 and 3. Figure 2 shows the grid pattern of response ratios for zinc. Zinc concentrations varied from <0.020mg/kg to over 6.0mg/kg measured in a single pass along with all other elements using the ICP-MS. Figure 3a shows the responses for gold, and Figure 3b illustrates the dataset truncated at 100 times the lowest response in order to investigate trends in the lower response ratio classes. Over all plots for the survey indicated anomalies for Au, Ag, Cu, Pb, Zn, Mo and Sb.

## DISCUSSION

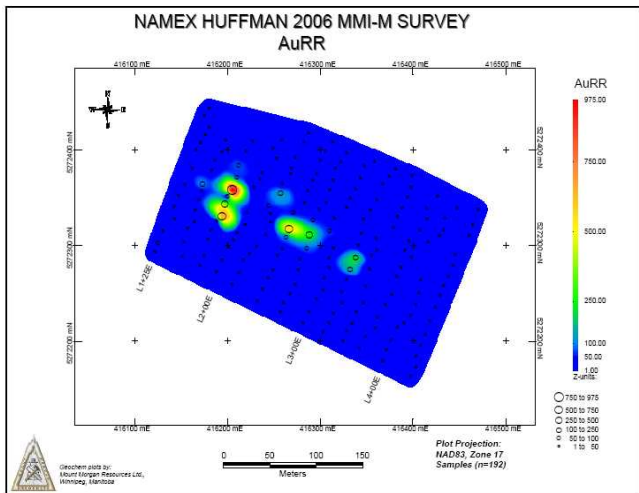
Interpretation of the data indicated that a 300m long by 200m wide geochemical anomaly is associated with fault-hosted high-grade Au, Ag, Cu, Pb, Zn, Mo and Sb mineralization that occurs on the property. The Huffman mineralization is associated with a felsic porphyry and is along strike from the past-producing Jerome Mine (Figure 1). The thickness of the overburden varies from 3-7m or more. There is very little information available regarding the age of the overburden but it is glacial till, locally reworked to produce a sand-silt layer of indeterminate thickness. There are also 'inliers' of lacustrine clay.



**Figure 2:** Response Ratios for Zinc, measured using MMI-M and the dual detector ICP-MS. Zinc values of up to 6.0mg/kg were measured in a single analysis



**Figure 3b:** Truncated Results for Au at 100 times the lowest response ratio, showing increased detail of Au distribution.



**Figure 3a:** Response Ratio Data for Gold using the MMI-M Selective Weak Extraction and ICP-MS analysis

There has been no geological mapping on the property to this point in time. However, the encouraging results from the MMI-M survey will be followed up in the near future by excavation of overburden, geological mapping and other investigative techniques.

Highly anomalous MMI-M responses of greater than 100 times background were quantitated using the dual detector calibrated ICP-MS to give information on over forty elements from which the conclusions were drawn. The ability to measure high concentrations of elements such as Zn (Figure 2) shows the advantage of the dual detector. In addition, the multi-element capability, where the high levels of elements can be determined simultaneously with lower amounts illustrates the power of the

ICP-MS to produce high quality data for a wide variety of elements in a single analysis. Furthermore, the truncated results for Au (Figure 3b) illustrate how the high sensitivity of ICP-MS can be utilized to obtain geological information at very low concentrations.

### CONCLUSION

There is an increasing need for high precision analyses of geological samples for a greater range of elements and concentrations. Modern exploration methods involve statistical analysis of data from a wide set of elements in order to assess possible ore deposits. The challenge for the analytical technique is to evolve to meet these ever-changing demands. These can include: the addition of more elements, lower detection limits, and increased ranges of concentrations. ICP-MS has been shown to provide reliable results for geological samples and the constant improvement in the technique only strengthens its applicability to a wide variety of situations for both now and the future.

### ACKNOWLEDGEMENTS

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**REFERENCES**

- Mann, A.W., Birrell, R.D., Mann, A.T., Humphreys, D.B. and Perdix, J.L., 1998. Application of mobile metal ion technique to routine geochemical exploration. *J. Geochem. Explor.* 61:87-102
- Riddle, C. (ed.), 1993. *Analysis of Geological Materials*. Marce 1 Dekker