Soil Sample Preparation, Analytical Techniques and QA/QC

Earth Sciences Sector

Rick J. McNeil
Robert G. Garrett
Natural Resources Canada - Geological Survey of Canada

Workshop on the Role of Geochemical Data in Ecological and Human Health Risk Assessment
Halifax, Nova Scotia, March 17-18, 2010

Objectives

Demonstrate the factors affecting the analysis of a sample and initiate discussions on defining an analytical protocol that will:

- *provide consistent data across North America and with the majority of the regulatory regimes*
- *provide data that are to the greatest extent possible compatible with current data holdings*
- *extend the methodologies developed over the past 30 years at the GSC during the URP, MDAs 1 and 2, MITE and TGIs*

Factors Affecting Geochemical Data

- Mineralogy *(not covered here)*
  - Primary distribution, effects of sediment erosion and transport, and soil formation *(weathering processes).*
- Sample preparation
  - Sample drying (temperature)
  - Grain-size fraction and efficiency of the size separation
- Sample analysis
  - Chemical digestion or other preparations
  - Analytical instrument used
  - Sample weight

North American Soil Geochemical Landscapes Project
Sample Preparation and Analytical Procedures *(Canadian Core Samples)*

Natural Resources Canada

Ressources naturelles Canada

Canada

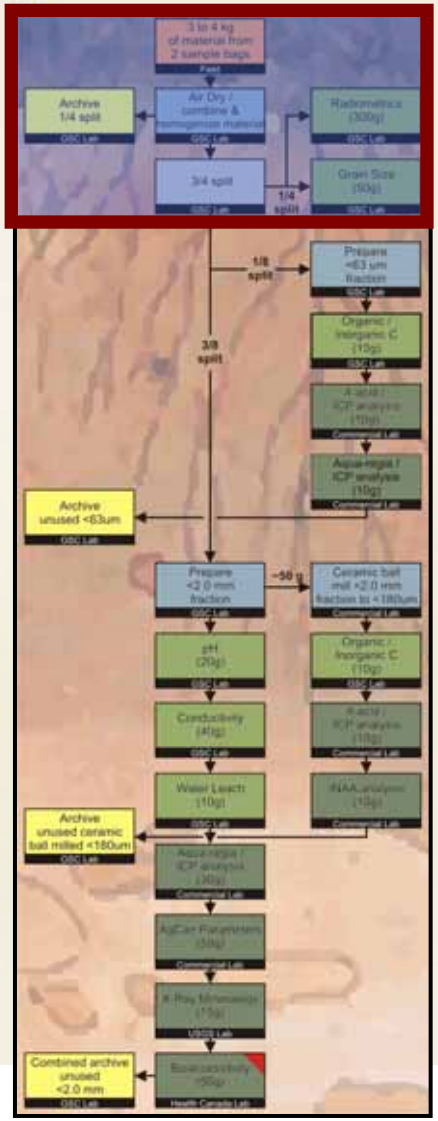
Sample Preparation

Sample Preparation

- **Sample collection**: *Analysis requires approximately 4 kg of field moist material.*
- **Sample drying:** *Air dried below 30 ℃; volatile elements such as Hg and As can be affected by higher drying temperatures*
- **Sample splitting:** *Sample is homogenized and split*
- **Sample archiving:** *Archive is approximately 500 g of dried material*

Sample Drying

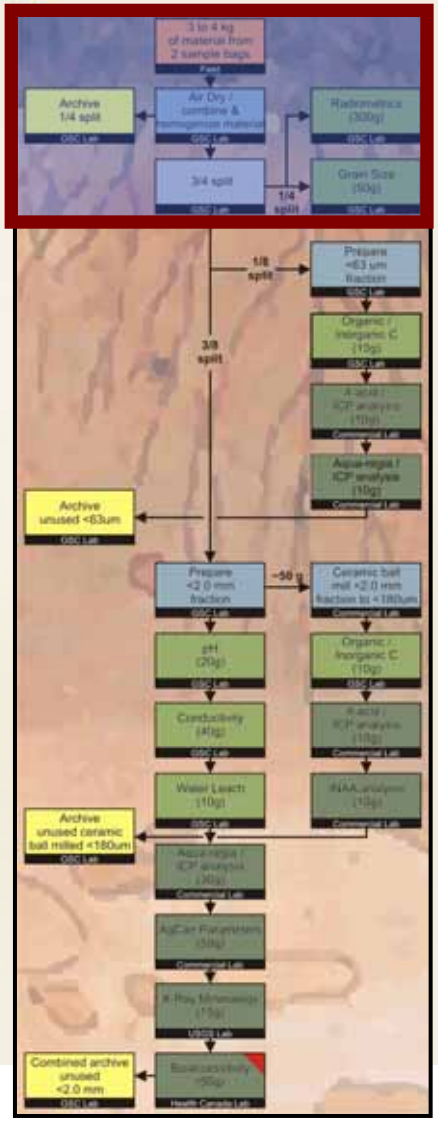
Sample Splitting



Sample Preparation

- **Pulverizing with a ball or ring mill**

  This procedure should not be used as part of sample preparation for purposes of risk assessment because the processing may bias final results. Such milling is used for total analysis (using the 4-acid digestion), not for samples to be treated with aqua regia and its variants, the water leach or other partial extractions. Although sample materials are dried and screened prior to chemical analysis, if not touched by pulverizing, the mineral fragments resistant to physical and chemical weathering are not disaggregated and, hence, remain closer to their natural state.



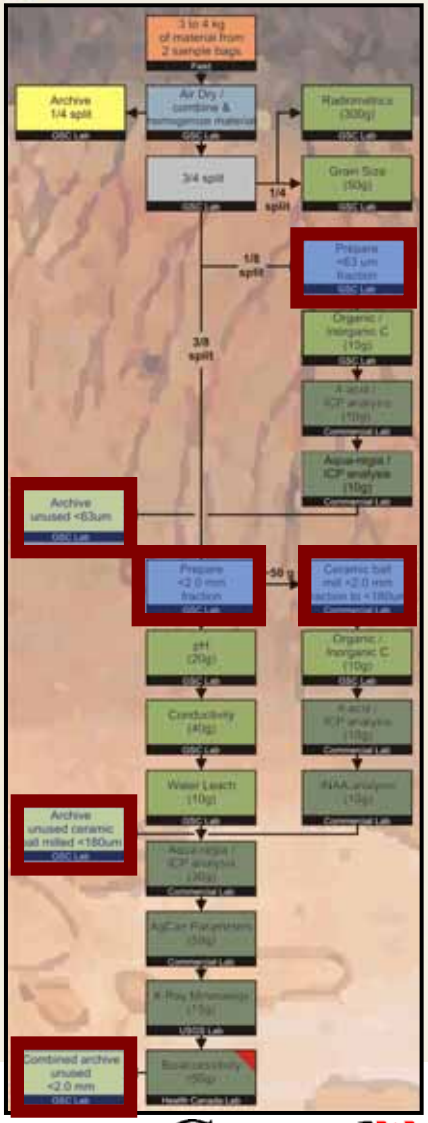
Sample Drying *Sample Splitting*

Sample Preparation

- **Sample sieving**: *Two size fractions are prepared*
  - ***<2 mm (all horizons)***
    - *~200 g of <2 mm material*
    - *~50 g of <2 mm material for pulverizing*
      - *Ceramic pulverized to <0.063 mm*
  - ***<0.063 mm (B and C-horizons only)***
    - *~25 g of material*
- **Sample archiving**: *Archive unused and excess prepared material*

Sample Sieving

Sample Archiving



Sample Analysis

- Geochemical data reflect the proportions of mineral and organic material in the sample, the concentration of the elements in those materials, and the ability of the acid to decompose the materials.

Always state the sample digestion AND the analytical technique: This describes the methodology, NOT the technique alone!

Sample Analysis

Considerations when choosing an analytical method

- Sample decomposition *(digestion)*
  - ***Total:*** Total value of elemental concentration in sample regardless of mineralogy and chemical speciation
  - ***Partial:*** Partial value of elemental concentration in sample is largely dependant on the mineralogy and the strength of the digestion method (potentially more insight on chemical speciation)
- Analytical technique
  - ***Destructive:*** sample is fully decomposed and discarded after analysis
  - ***Non-destructive:*** sample can be reused after analysis
- Elements and detection limits
  - Does the analytical technique have lower and upper detection limits required for specific elements of interest? Is it 'fit for purpose'?
- Grain size
  - It is important to recognize that different grain size fractions may have different mineralogical compositions and increased grain surface area as the size fraction decreases
- Sample size
  - How much material is necessary for a representative analysis of the whole sample, and to reduce the possibility of any "nugget effect"

Sample Decomposition
(Partial)

Aqua Regia *(classic):* 3:1 HCl: HNO_3

Aqua Regia *(modified EPA3050B) variant*: 4:1 HCl: HNO_3

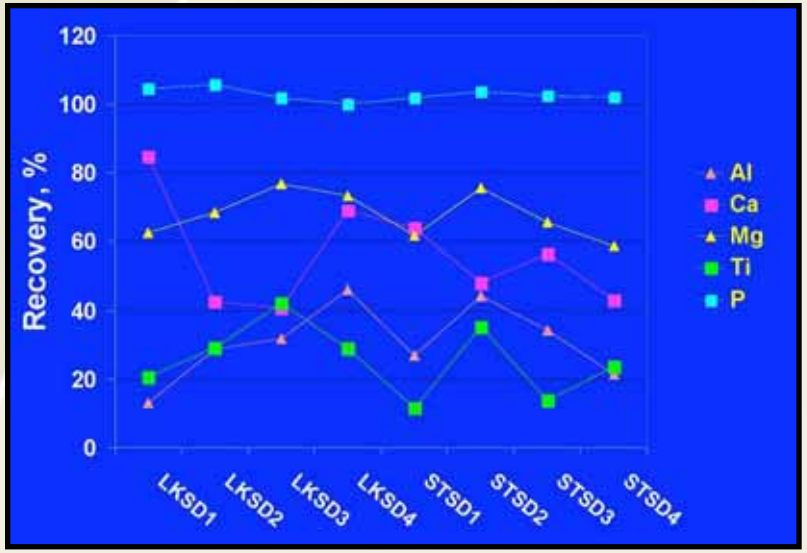
Minerals attacked *(partially / totally dissolved):*

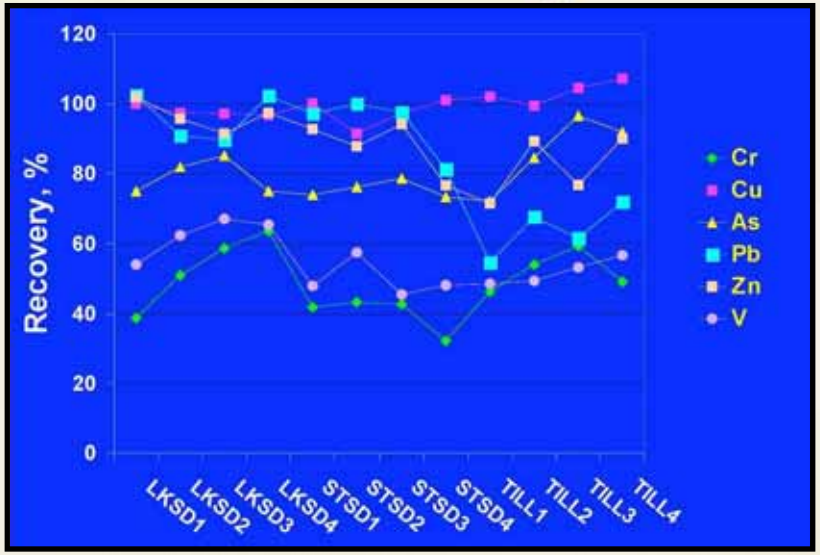
- *sulphides*
- *arsenides*
- *phyllosilicates*
- *native Au*
- *most sulphates*
- *organically bound elements*
- *carbonates*
- *selenides*
- *Pt, Pd*
- *tellurides*
- *some oxides (Fe-Mn oxides)*

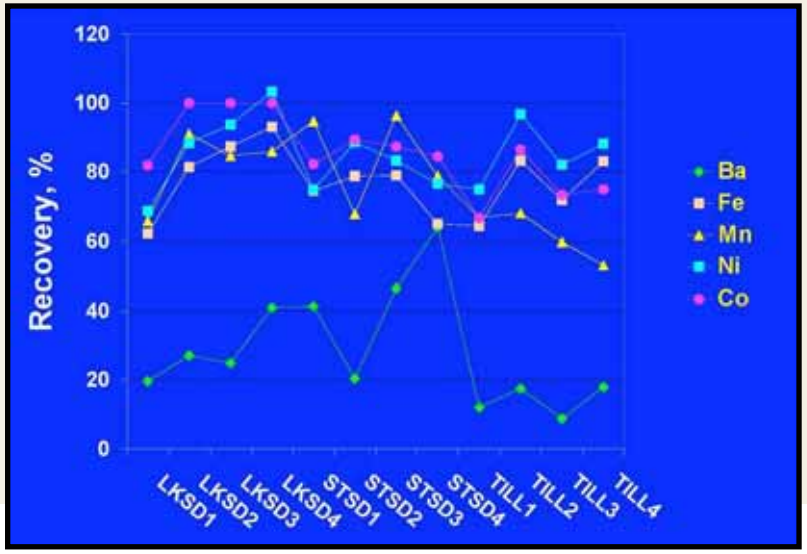
Minerals weakly attacked *(not fully dissolved):*

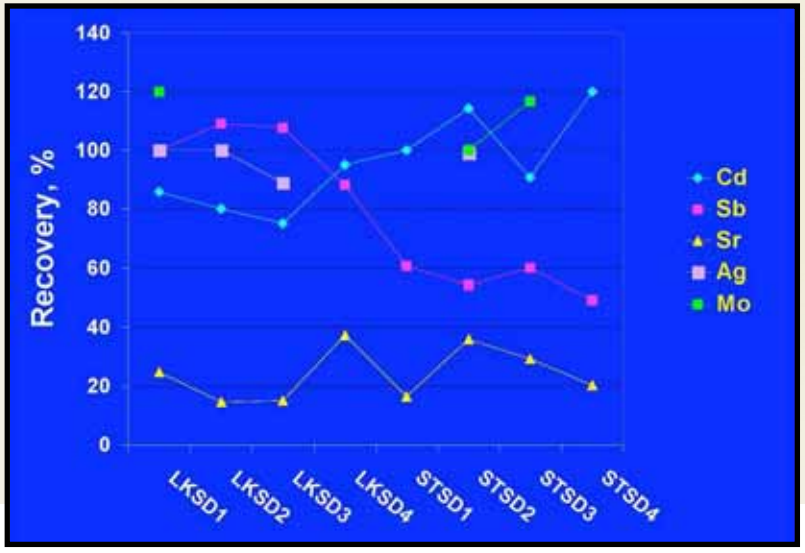
- *barite*
- *cassiterite*
- *amphiboles*
- *zircon*
- *chromite*
- *feldspar*
- *sphene*
- *garnet*
- *quartz*
- *ilmenite*
- *monazite*
- *gahnite*
- *rutile*
- *pyroxenes*

Recovery in Aqua Regia









Hall (2007)

Aqua Regia Variant Study

Study was conducted using 8 different control reference material digested in 5 different Aqua Regia variants

CRMs:

1- LKSD-1

2- LKSD-4

3- STSD-1

4- STSD-4

5- Till-1

6- Till-4

7- SoNE-1

8- 2711

"Aqua Regia" digestion

1- (AR1111) 1:1:1 HCl-HNO_3-H_2O

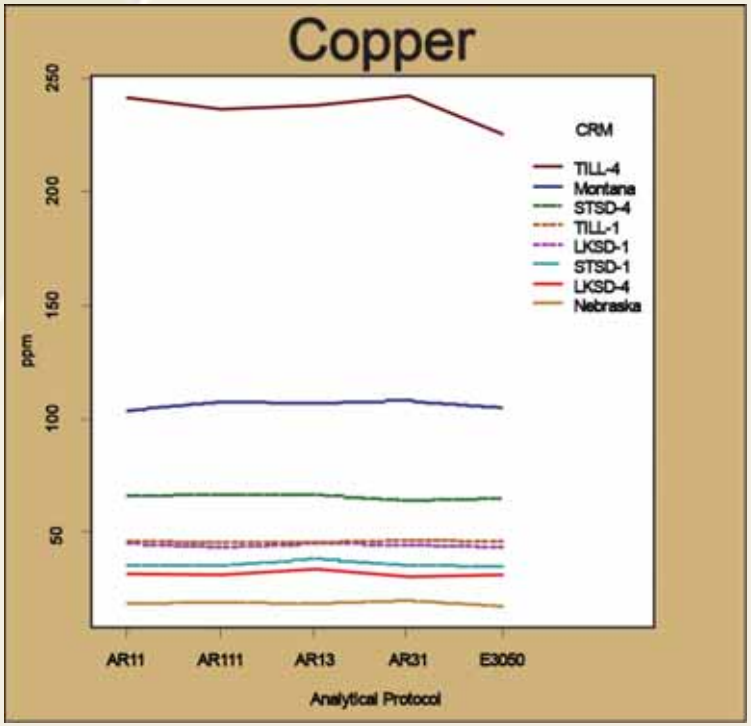
2- (AR311) 3:1 HCl-HNO_3 [classical Aqua Regia]

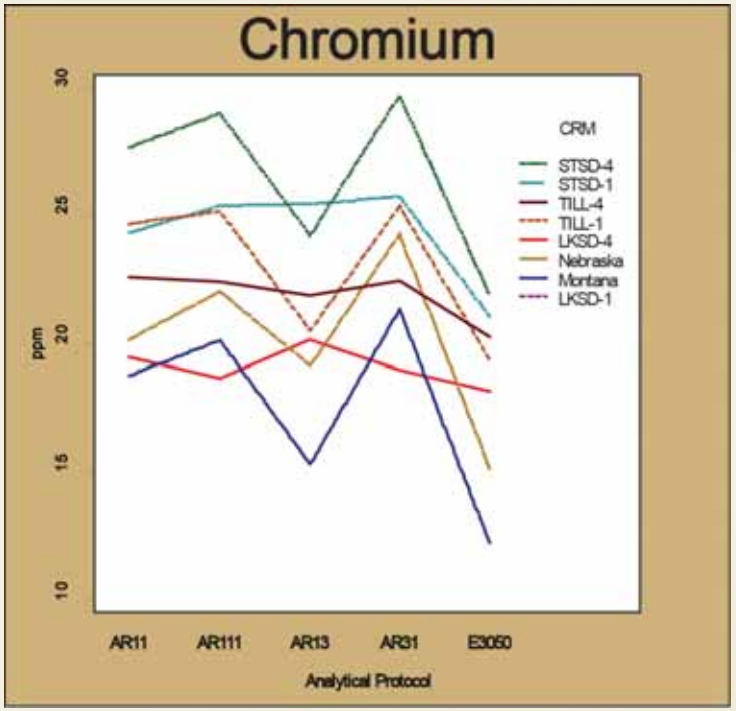
3- (AR131) 1:3 HCl-HNO_3 [Lefort, reverse Aqua Regia]

4- (AR112) 1:1 HCl-HNO_3

5- (US-EPA 3050B) HNO_3-H_2O_2 variant, E3050

Aqua Regia Variant Study





Test results show that:

- US-EPA3050B generally extracts less metals, with the exception of Hf, Nb, Th and Zr
- Other Aqua Regia variant results are generally similar to copper
- Overall the Aqua Regia digestion yields very consistent results for most elements

Garrett et al. (2008)

Sample Decomposition
(Near total)

"Four-acid": HF - $HClO_4$ - HNO_3 - HCl

Minerals attacked:

Stronger attack than Aqua Regia dissolving most minerals

Minerals hardly attacked:

Similar to Aqua-regia but REEs, Al, Ba, Ta, Nb, Hf, Sn, Cr, W, Fe still may not be total.

Si volatilises, as does Cr, As, Sb, Au sometimes (dependent on conditions)

Sample Decomposition
(Partial)

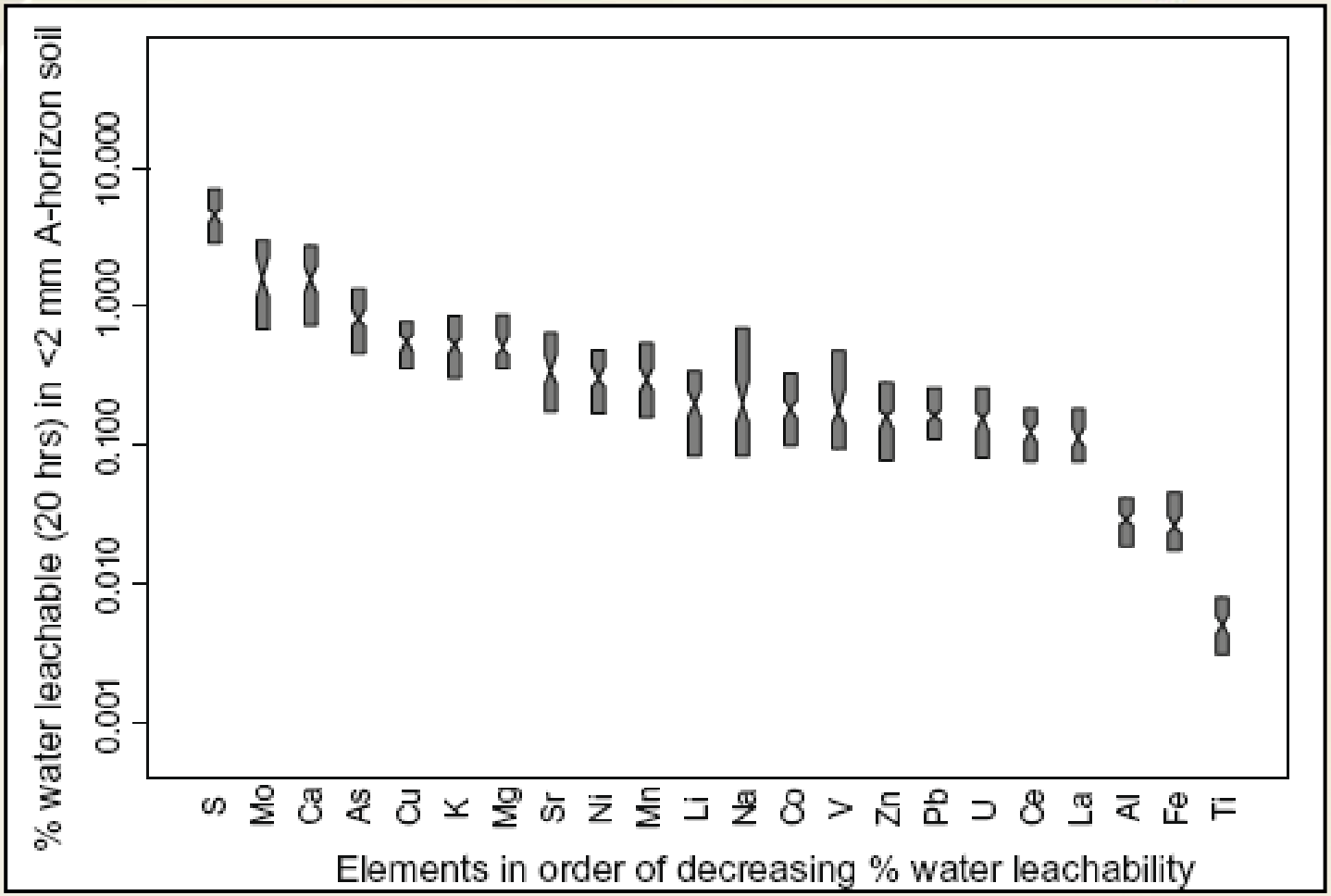
Water leach: Reverse osmosis – Deionized water (RO-DI)

- Use of this weak leach provides relevant data more closely related to bio-accessible concentrations of elements in soil compared to other methods

- Ensures the pH of the extraction is controlled to a large degree by the sample itself and results should reflect that portion of an element most likely to be mobile under ambient conditions

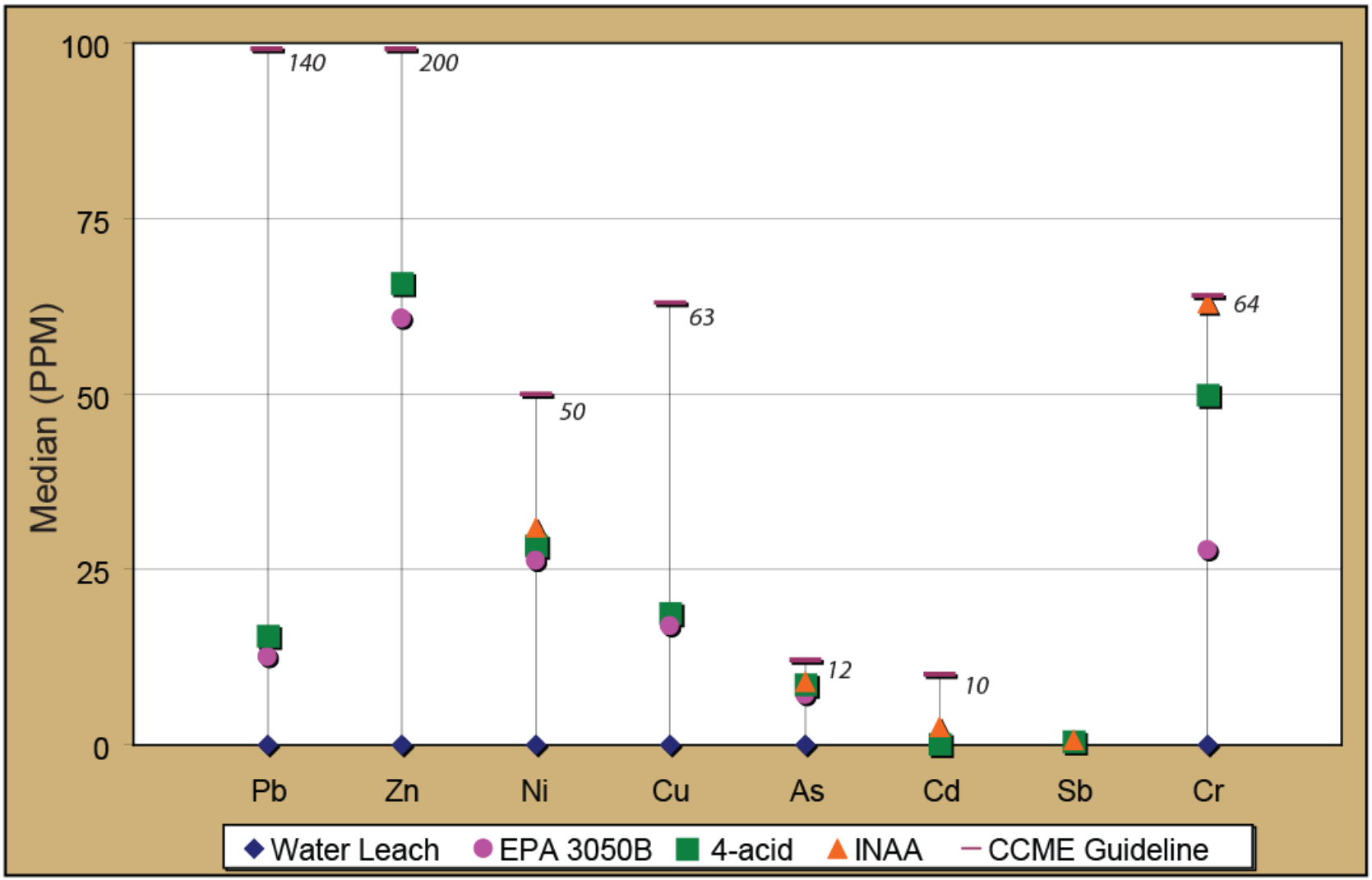
Garrett et al. (2009)

% Water Leachable



Garrett et al. (2009)

Maritimes C-horizon <2 mm



Analytical Techniques

Commercial labs include multi-element ICP-OES, ICP-MS, INAA and AAS packages that are well suited for the determination of most trace, minor and major elements. *However, each method does not provide reliable results for all elements because of elevated detection limits for some methods.*

- **Common techniques include:**
  - **ICP-MS** (Inductively Coupled Plasma-Mass Spectrometry)
  - **ICP-OES** (Inductively Coupled Plasma-Optical Emission Spectrometry)
  - **INAA** (Instrumental Neutron Activation Analysis)
- **Other techniques not covered here:**
  - **AAS** (Atomic Absorption Spectrometry)
  - **XRF** (X-Ray Fluorescence)
  - **Element specific technique** (e.g., ion specific electrode (ISE))

Analytical Techniques

ICP-MS (Inductively Coupled Plasma – Mass Spectrometry

(mostly trace elements because too sensitive for major components)

Advantages:

- Multi-element technique suitable for wide range of elements to sub-ppb DLs.
- Ideally suited for ultra-trace geochemical methods such as selective and sequential extractions, waters, vegetation
- Most spectral interference can be negated by appropriate operating conditions

Limitations

- The total dissolved salt content of the analyte solution must be kept low or instrument performance is adversely affected; dilution can lead to inadequate DLs for some elements
- Technical expertise is required to mitigate spectral and non-spectral matrix effects
- Ultrapure acids are required for leaches and digestions, thus increasing the cost of analysis

Analytical Techniques

ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry) *(mostly major elements because of lack of sensitivity)*

Advantages:

- Multi-element technique suitable for wide range of elements to ~ppb DLs.
- Instruments are robust and relatively inexpensive, operation and methods are well documented
- Most spectral interference can be negated by appropriate operating conditions
- Cheaper per analysis than ICP-MS

Limitations

- Less sensitive than ICP-MS, should be used as a complementary technique for the same digested sample

Detection Limit Ranges

Aqua-Regia
ICP-MS/ICP-OES

Detection Limits

- <0.001 ppm
- 0.01 - 0.001 ppm
- 0.1 - 0.01 ppm
- 10 - 0.1 ppm
- >10 ppm

1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON
37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
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87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM		114 (289) Uuq UNUNQUADIUM				

LANTHANIDE

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

Analytical Techniques

INAA (Instrumental Neutron Activation Analysis)

Advantages:

- Simultaneous, multi-element, total, automated technique that does not require digestion and therefore there is little likelihood of contamination
- Interferences (not too many) are well documented
- Good precision and accuracy
- No volatilization of As, Hg and Sb, as is potentially the case with the “near-total” 4-acid digestion
- Sample weight up to 30-40 g

Limitations:

- There is not enough coverage of the Periodic Table at adequate detection limits
- Limited number of nuclear reactors offering service
- Does not give any indication of the bio-accessible portion of the sample

Detection Limit Ranges

INAA

Detection Limits

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Analytical Techniques

Selective Extractions

- These remove metals held in successively more "fixed" forms *(e.g. Hall, et al., 1996).*

- They are used to estimate metal residence in different mineral forms and compounds, and can determine metals either bound on, or co-precipitated with: 1) clay, 2) organic material, 3) iron or manganese oxy/hydroxides, and 4) carbonate or weakly dissolved salts.

- Can answer a question – gives some insights into speciation and where elements reside with respect to mineral phases, and hence, could be easily available or totally inert, e.g. chromium in fuchsite vs. chromium in chromite

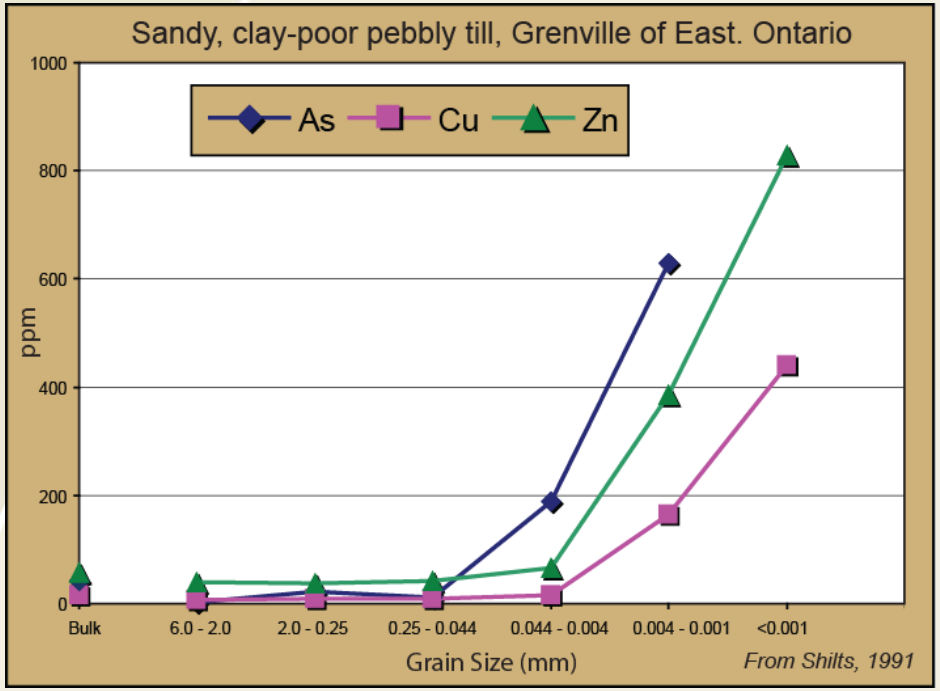
Grain Size and Chemical Partitioning

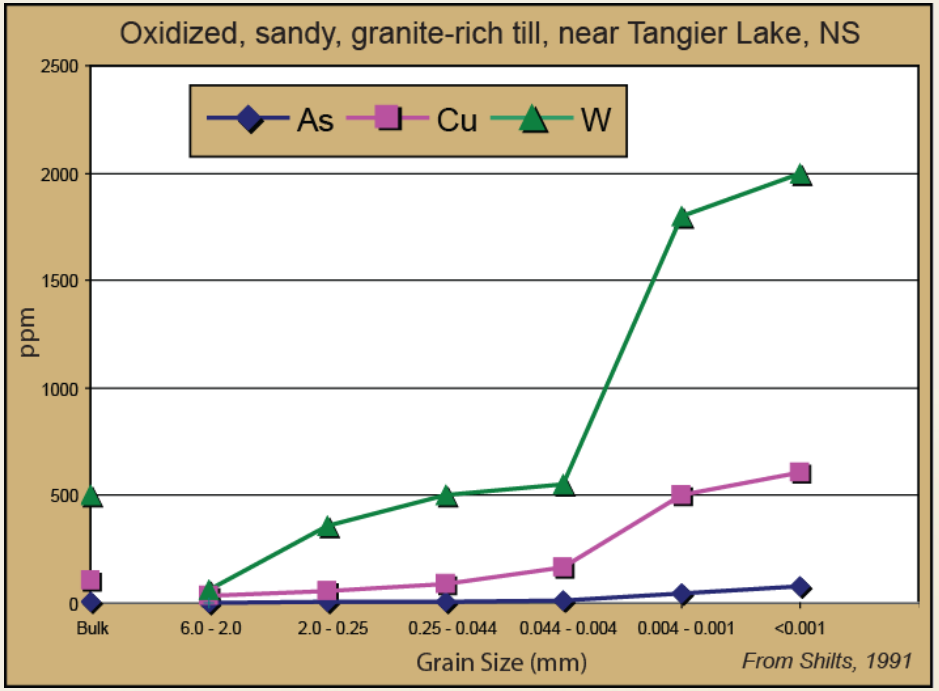
- The size distribution of minerals or rock fragments is primarily a function of their physical properties;
  - *Micas, chlorite and other soft or cleavable minerals predominate the fine fraction*
  - *Quartz, spinel and other hard, non-cleavable minerals dominate the coarser sand fraction*

- It is necessary to recognize the possible geochemical effects of chemical partitioning by grain size and the effects of weathering on labile components

- This physical, mineralogical partitioning translates geochemically into chemical partitioning for the obvious reason that the size fractions dominated by certain mineral phases will reflect the chemical make-up of those phases. *Shilts (1991)*

Grain Size and Chemical Partitioning





Grain size classes:

6.0 – 2.0 mm: almost wholly composed of rock fragments
2.0 – 0.25 mm: mixture of rock fragments and mineral grains
0.25 – 0.044 mm: sand and coarse silt; almost wholly mineral grains dominated by quartz and felspar (usually 90%)
0.044 – 0.004 mm: silt; mineral grains dominated by quartz and feldspar
0.004 – 0.001 mm: clay; mineral grains dominated by phyllosilicates and other soft minerals
<0.001 mm: clay and colloidal particles

Grain Size and Chemical Partitioning

- Selection of grain-size fraction for analysis is based on the needs of the geochemical survey
- <2 mm fraction is a standard for agricultural and environmental studies
- Silt plus clay-sized (<0.063 mm) or the clay-sized (<0.002 mm) is traditionally used mainly for mineral exploration and geological research
- Use of the finer size fractions can potentially provide more information on bioaccessibility

Size fractions used by government departments

Environment Canada: <2 mm

Health Canada: <2 mm

Agriculture Canada: <2 mm

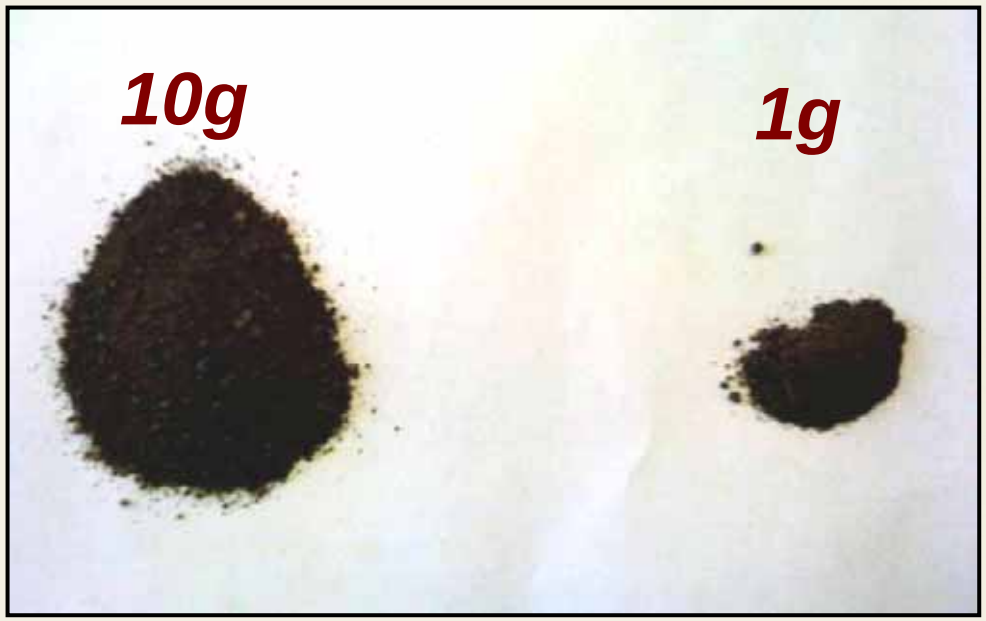
Natural Resources Canada: <2 mm, <0.063 mm and <0.002 mm

Other provincial agencies: <2 mm

Sample Size

The larger the sample weight the more it:

- Will be representative of the whole sample
- Will reduce the potential for any “nugget effect”
- Will yield better analytical reproducibility



Ensuring Quality

It is the responsibility and professional duty of an investigator to ensure the quality of the analytical data independently from a service laboratory

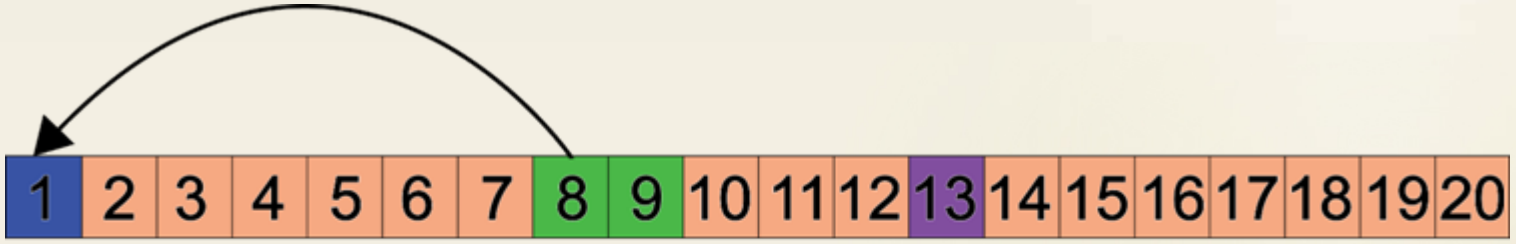
How?

- By inserting “blind duplicates” into the submitted samples to estimate analytical reproducibility – precision, and
- By inserting samples of bulk “control reference materials” into the submitted samples to check on long-term consistency
- Insertion of internationally or nationally certified “control reference materials” will facilitate between-study comparisons, and may be important in some regulatory situations
- By monitoring the laboratory results and working with the laboratory to ensure the data have adequate quality

Ensuring Quality

Samples are collected in blocks of 20 samples (001-020, 021-040,...)

- 17 Routine Sites
- 1 Control Reference Position
- 1 Blind (analytical) Duplicate Position
- 1 Field Duplicate



2	Routine sample
1	Blind duplicate
8	First field duplicate
9	Second field duplicate
13	Control Reference

Blind Duplicates

Blind duplicates should be inserted at regular intervals in a batch of samples submitted for analysis. A practical frequency is 1 in 20, a 5% overhead

Operationally:

- It is often convenient to place the analytical duplicate into the first position of a block of 20 samples. It will be a "split" from the prepared material for one of the following field samples. The laboratory does not know which one, and does not have the time to find out if it is running a profitable service

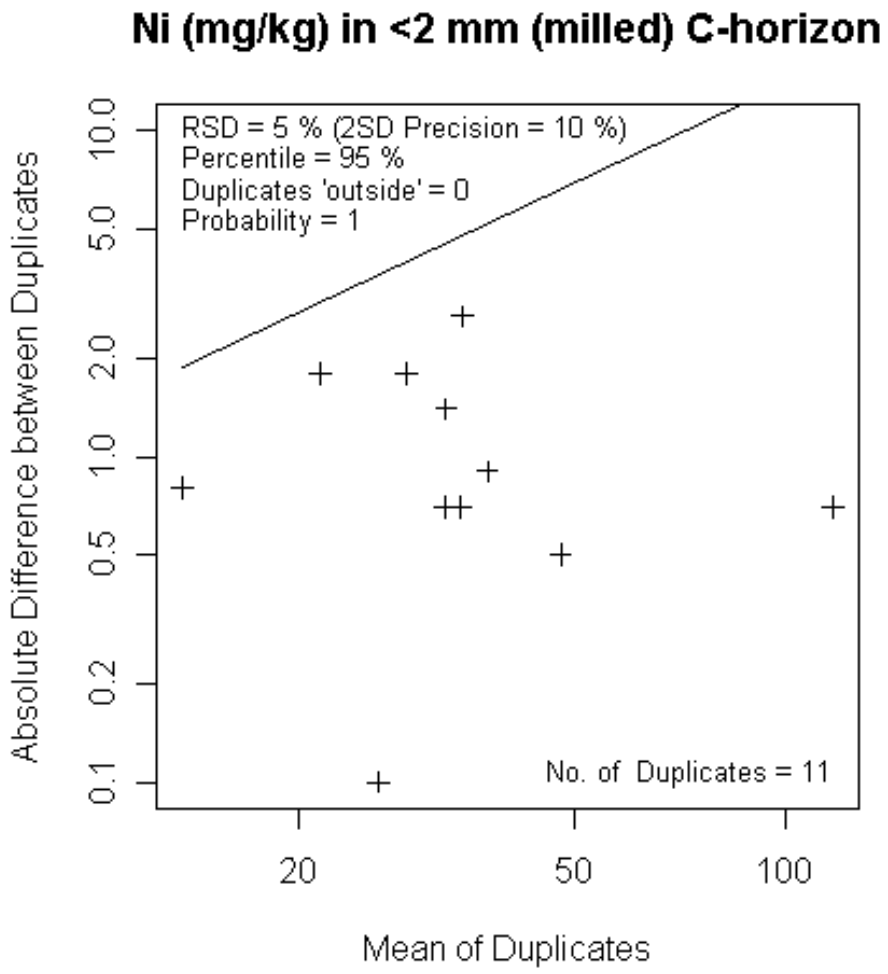
- The duplicate analyses are checked to see if they fall within pre-established tolerance limits, i.e. within a particular range the results should agree within a stated percentage

- Tolerance limits will be more "relaxed" close to the detection limit due to the inherent instrument problems at those levels, and

- Results can be plotted and monitored on Thompson-Howarth plots, and further evaluated for "fitness for use" by ANOVA

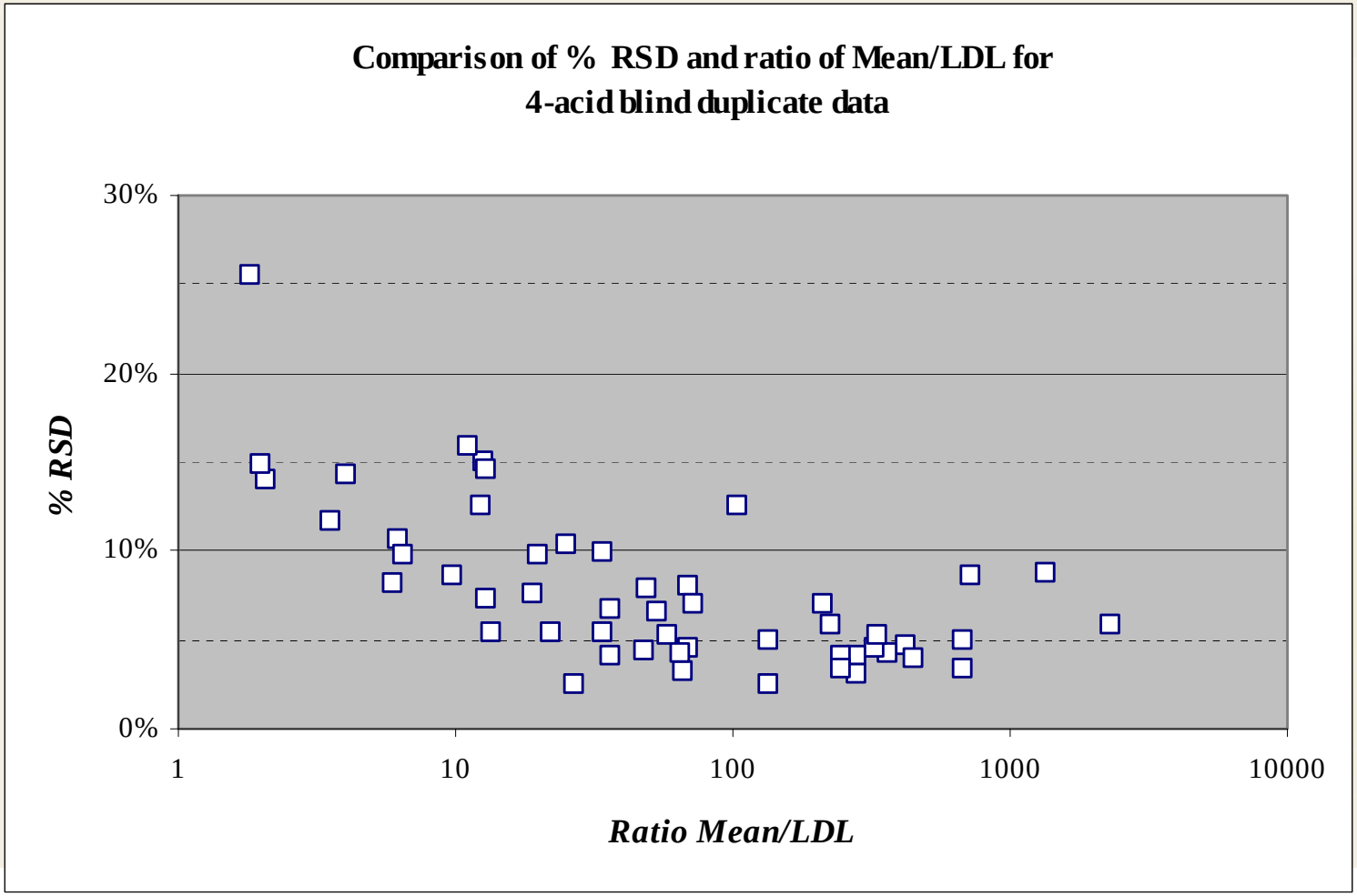
Blind Duplicates

The Thompson-Howarth plot:



Blind Duplicates

The relationship to the detection limit:



Control References

Control Reference Material (CRM) samples should be inserted at regular intervals in a batch of samples submitted for analysis. A practical frequency is 1 in 20, a 5% overhead

Operationally:

- It is advisable to use more than one CRM, as much as possible they should be similar materials as those being submitted for analysis and should span the expected range of the results

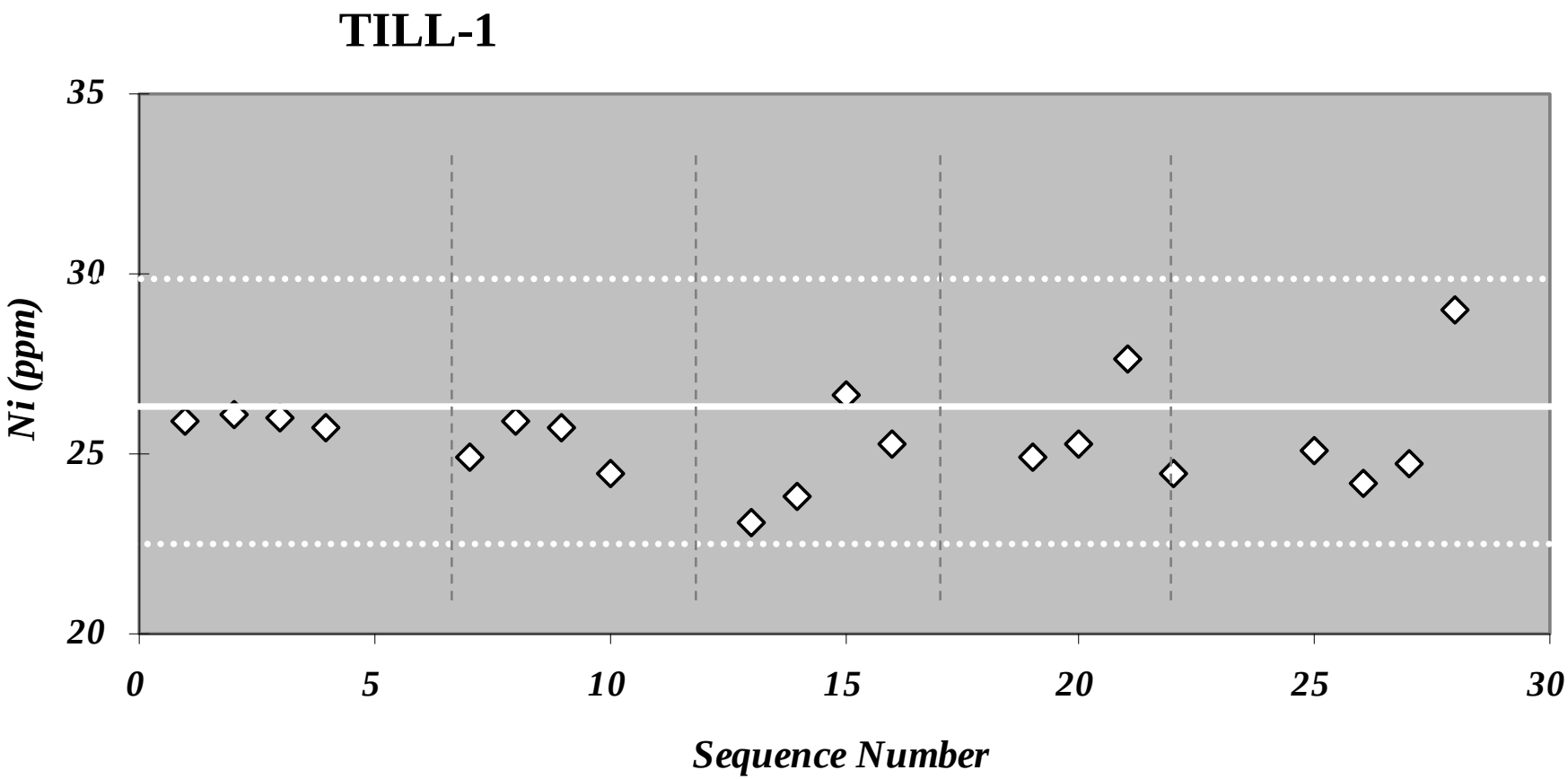
- Too many CRMs and they do not occur frequently enough to effectively monitor for analytical drift, on large projects 3 or 4 are appropriate

- Tolerance limits will be more “relaxed” close to the detection limit due to the inherent instrument problems at those levels, and

- Results can be plotted on X-charts, and precisions (RSDs) can be estimated for the concentrations the CRMs represent

Control References

An X-chart:



Recommendations

- Know what you need to know from the analytical data as many variables affect the geochemical numbers:
  - sample decomposition *(mineralogy)*
  - analytical technique *(detection limits and reliable data for the elements)*
  - grain size *(mineralogy)*
  - sample weight *(representivity and reproducibility)*
- Based on results, GSC recommends the use of the US-EPA 3050B Aqua Regia variant – it is commonly used and it does the job
- Is any one better ? Not necessarily, but there is a need for consistency to enable comparison between studies and regulations and US-EPA 3050B is commonly used
- Do not forget the QA/QC, data quality is your responsibility
- Work with the laboratory as required to achieve the desired quality

Recommendations

Analytical Method Recommendation

Chemical digestion: US-EPA 3050B Aqua-Regia variant

Analytical technique: ICP-MS/ICP-OES

Grain size: <2 mm

Sample weight: 10 grams

QA/QC: insert blind duplicates and control references at 5% frequency, monitor the results, and work with the laboratory to achieve data quality objectives

Key to Abbreviations

- **URP** - Uranium Reconnaissance Programme
- **MDA** – Mineral Development Agreement
- **MITE** – Metals in the Environment
- **TGI** – Targeted Geoscience Initiative
- **ISE** – ion specific electrode
- **DL** – detection limit

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