Brenda Caughlin

Selective leaches - laboratory analysis

Selective Leaches - Laboratory Analysis

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Objective of selective leaching

- map specifically that fraction of an element which was was previously in a labile (free) form (derived from buried mineralisation) and has been 'trapped' or immobilised in the surficial environment
- no consensus on dominant mechanisms of transport of elements from mineralisation at depth
- general agreement principal resident sites in secondary environment for these migrating elements comprise hydrous Fe and Mn oxides, humic and fulvic components of humus materials, and clay minerals.

G.E.M. Hall (1998). J. Geochem. Explor. 61:1-19.

How Selective are Selective Leaches

- Binding mechanisms to phases unknown.
  - physical and chemical adsorption at surfaces
  - occlusion within structures
  - chelation
  - complexation
  - coprecipitation
- True specificity is not possible so selective leaches are "operationally defined"

"Operationally" Defined

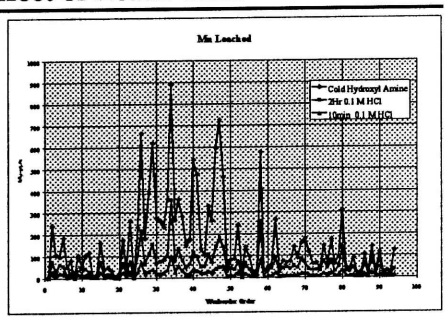
- "Operationally" defined methods require careful attention to a number of details to ensure consistent results within laboratories and between laboratories.
  - Explicit definition of Leach Conditions
  - Comparison of results with other workers - necessary because certified reference materials are not available
  - Careful control of leach conditions and instrumental analysis

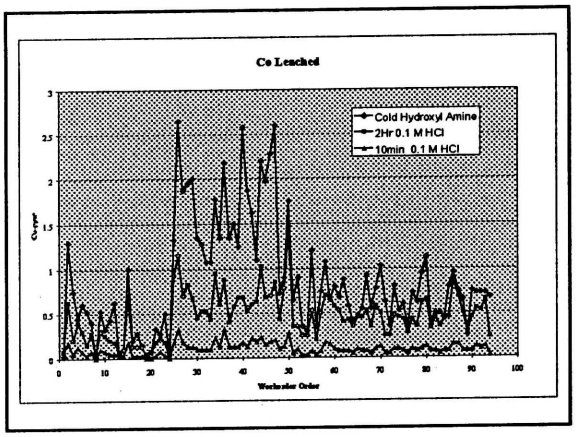
Define Leach Conditions

- Consistent results will require clear definition of leach conditions.
- "Room" Temperature Hydroxyl amine Leaches
  - » 0.1 M NH2OH-HCl in 0.01 M HNO3
  - » 0.1 M NH2OH-HCl / 1 M NH4OAc
  - » 0.1 M NH2OH-HCl, pH 2.5
  - » 0.1 M NH2OH-HCl, pH 4.5

  Hall (1996) J. Geochem. Explor. 56:59-78.
- Other variables include
  - Sample to Volume Ratio - 1g:20ml, 1g:50 ml
  - Time - 2 hours, 30 minutes, 10 minutes
  - Mixing during leaching

Effect of Leach Time



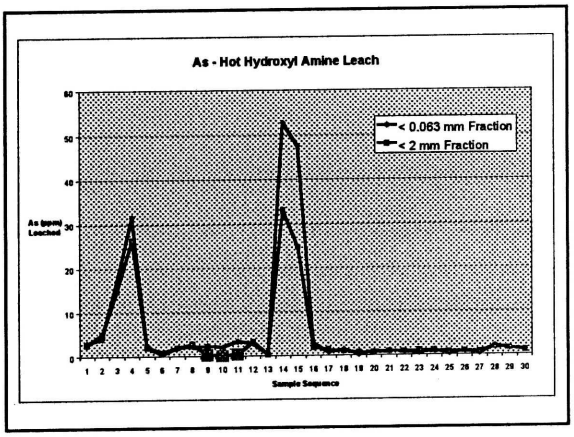


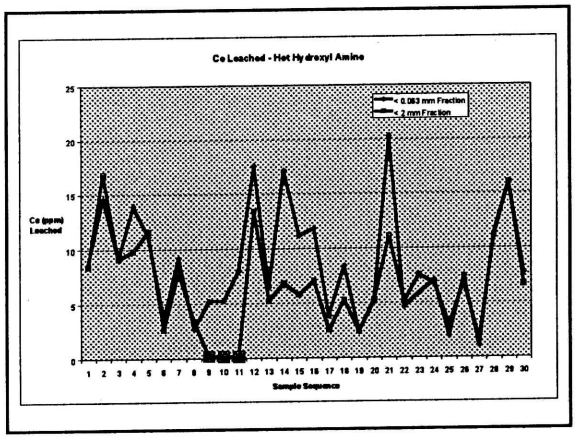
Factors Affecting Solubility

- The solubility of analytes in the leach solution depends on a number of factors.
  - Temperature
  - Nature of Solvent
  - pH
  - Common-ion Effect
  - Diverse-ion Effect
  - Hydrolysis
  - Complexes
- The leach solution AND the sample matrix influence these factors during the leach process

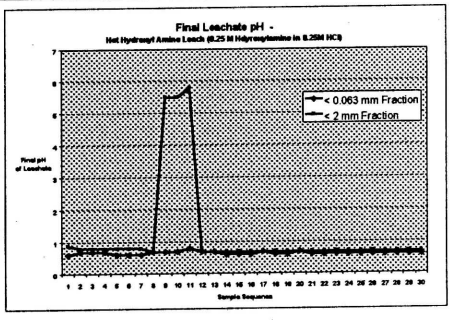
pH Critical Factor

- pH is a principal determinant of both primary mineral reaction rates and secondary mineral solubility
- sufficient alkaline species in samples will significantly alter the pH of the leachate solution changing the chemistry of the leach and impacting the intrepretation of the results
- most common rock forming minerals are capable of producing some alkalinity, but in widely varying reactions and rates.





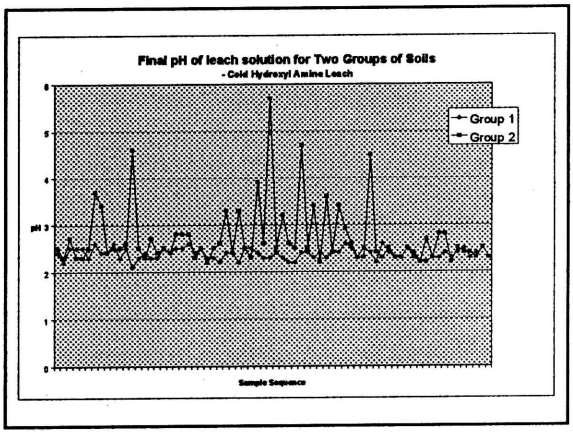
Monitor Final pH of Leachate



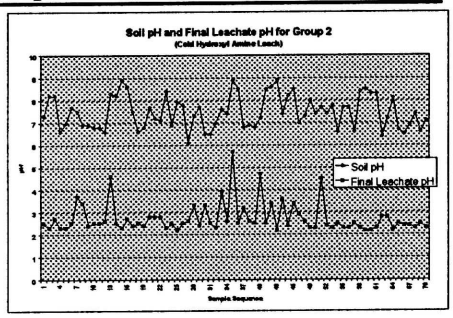
Neutralization Potential of Sample

- Soil pH measurements of the two fractions did not show significant differences. Neutralization potential is different.

	<2 mm	< 0.063 mm
Paste pH	8.1	7.8
pH - 1:1, 1 hour leach	8.1	7.8
pH - 1:100, 1 min leach	9.9	9.4
Neutralization Potential kg of CaCO3 equivalent / t of sample	380	124



Soil pH versus Final Leachate pH

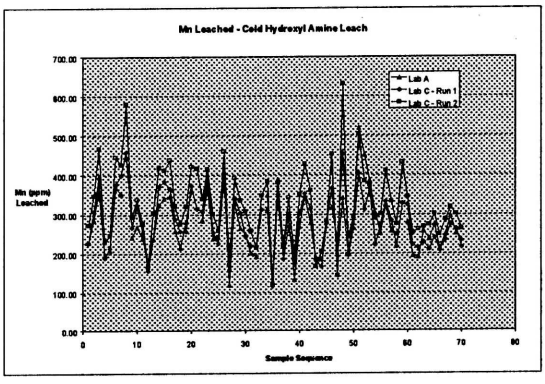


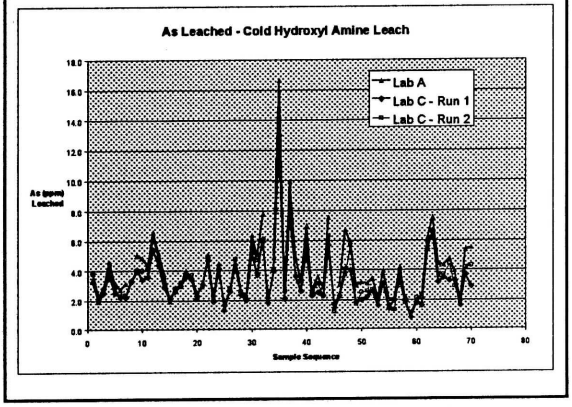
Comparability

- "Comparability - The confidence with which one data set can be compared to another"

  Taylor (1987) Quality Assurance of Chemical Measurements. Lewis Publishers, New York.

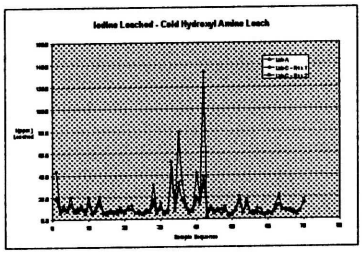
- For operationally defined procedures strict definitions of conditions and consistency in the execution of method is critical if results from lab to lab (or sometimes even batch to batch) are to be compared.





Calibration Difference

- Calibration issues identified and resolved through comparison / duplicate study

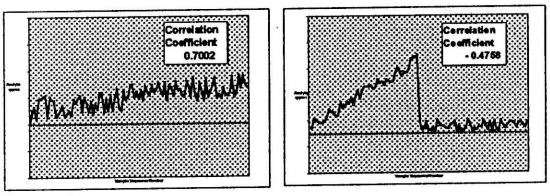


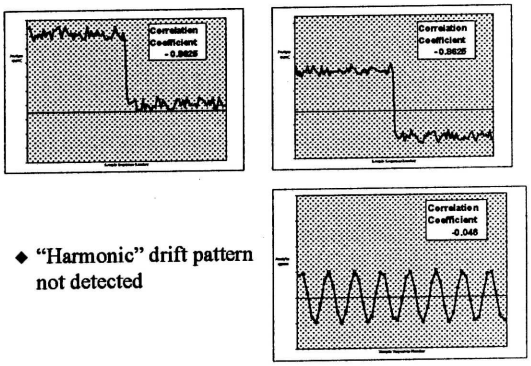
Calibration "Drift"

- Randomize samples before analysis
- Results for samples should have no systematic trends with respective to sample sequence number
  - Determine correlation between sample concentration and sample sequence number
  - Drift or sequence effects will be indicated by correlation coefficients 'close' to 1 and -1.

Simuluated Drift Data

- Drift patterns simulated with random noise



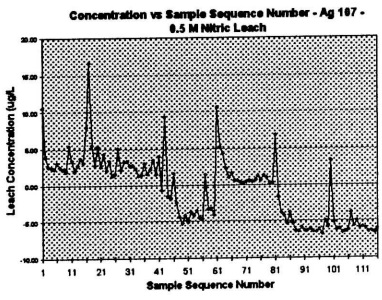


- "Harmonic" drift pattern not detected

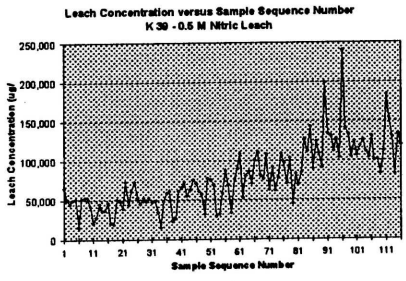
Drift Coefficients - 0.5 M Nitric Leach

Element	Coefficient	Element	Coefficient
Ag 107	-0.72	Co 59	0.01
Al 27	0.02	Cr 52	0.44
As 75	0.12	Cs 133	0.19
Ba 137	0.08	Cu 65	0.07
Br 79	0.25	Fe 57	0.69
Ca 43	-0.11	Gd 160	-0.15
Cd 112	0.53	I 127	-0.42
Ce 140	0.11	K 39	0.78
Cl 35	-0.11	Li 7	0.04

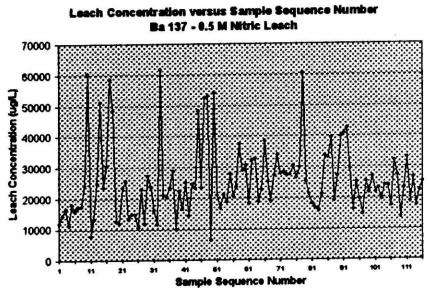
Ag Correlation Coefficient - 0.72



K Correlation Coefficient 0.78



Ba Correlation Coefficient 0.08

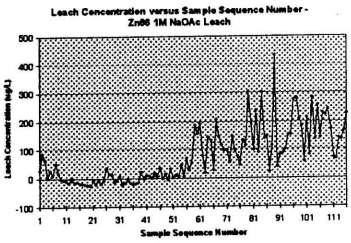


Drift Coefficients - NaAOc Leach

Element	Coefficient	Element	Coefficient
Ag 107	0.26	Ti 47	-0.21
Al 27	0.32	Tl 205	0.44
As 75	0.18	Tm 169	-0.53
Au 197	-0.10	U 238	-0.43
Ba 137	-0.11	V 51	0.30
Be 9	0.38	W 184	0.26
Bi 209	0.44	Yb 172	-0.50
Br 79	-0.40	Zn 66	0.70
Ca 42	-0.11	Zr 90	0.36

Zn - Correlation Coefficient -.70

Randomization problem not instrument drift. A Horizon and B Horizon soil sequences randomized separately within batch



Detection Limit

- Defined as the concentration of analyte producing a signal three times the standard deviation of the blank
- Procedural blank (all reagents without any samples) taken through the entire method used to determine detection limits

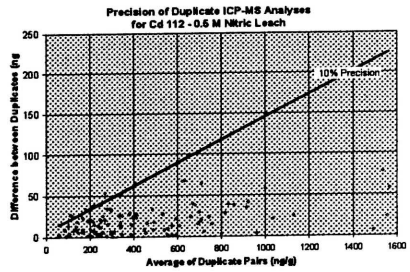
Detection Limits (ng/g) for Different Selective Leaches

	0.5 M Nitric	1 M NaOAc	0.25 M NH2OH.HCl
Ag 107	22	143	108
As 75	99	270	399
Au 197	7	78	12
Ba 137	260	202	1411
Bi 209	10	8	10
Br 79	190	2400	2700
Cd 112	4	59	10
Ce 140	40	7	93
Cl 35	2300	6300	
Co 59	25	27	25
Cr 52	29	1500	725
Cs 133	1	11	3
Cu 65	196	248	574

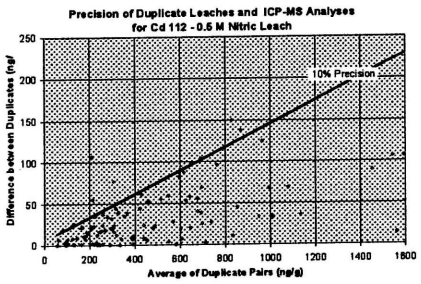
Analysis of Duplicate Pairs

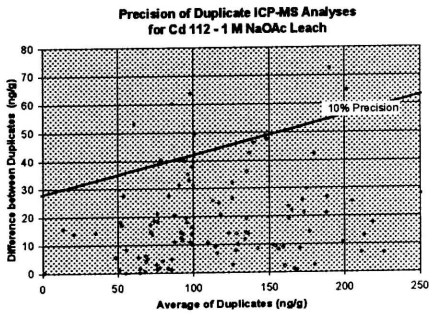
- Duplicate determinations can be used to access the precision and detection limit of analytical procedures.
- Duplication takes into account the variation in sample matrix and analyte concentration.

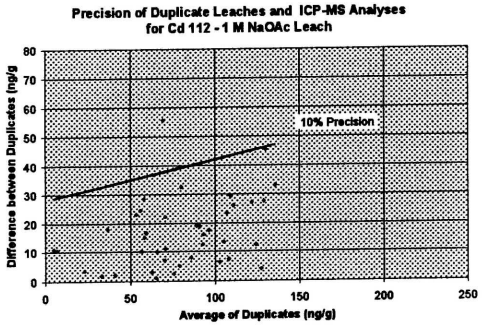
Duplicate Precision of Instrument



Duplicate Precision of Leaching







Multi-Element QC

- For *n* analytes where the error on each is independent, the probability that all results will fall within their respective 95% confidence limits is the probability that all results will be within 95% confidence levels is $(0.95)^n$
- For 50 elements, $(0.95)^{20} = 0.0769$
- One or more analytes will be "out of control" over 90% of all batches

Probability of Failures

- Table of the binommial probability of M points (elements) out of N points (total elements determined) will fall above the 95th percentiles

# Failures out of 50	Probability
1	0.9231
2	0.7206
3	0.4595
4	0.2396
5	0.1036
6	0.0378
7	0.0118
8	0.0032