How, What and Why of Assaying

Presented by

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SMITHERS, BC - APRIL, 2008
How, What and Why of Assaying

Topics

- Some Definitions
- The Analytical Process
  - Preparation
  - Digestion
  - Determination
- Ensuring Quality
  - Measures taken by the Lab, Certification
- Your Survey
  - Matching needs to budgets
  - Designing your survey
  - First Contact with the Lab
  - Submitting samples to the Lab
How, What and Why of Assaying

Definitions

- **Analyte**: An element or compound
- **Assaying**: Generic term for analysing a sample for one or more analytes
- **Assay**: The analytical process of determining one or more analytes with a high degree of accuracy and precision
- **Geochemical Analysis**: The analytical process of determining one or more analytes with a moderate degree of accuracy and precision
- **Detection Limit**: Lower limit at which an analyte can be measured with precision of ±100%
- **ppm**: Analyte concentration equal to one part in one million (1:1,000,000) on a weight to weight basis
- **ppb**: Analyte concentration equal to one part in one million (1:1,000,000) on a weight to weight basis
How, What and Why of Assaying

Definitions

- **Accuracy**: The trueness of an analytical measurement.
- **Precision**: The repeatability of an analytical measurement.
Analytical Process

Objective: Report the concentration of one or more analytes with an acceptable degree of precision and accuracy within the presented materials.

Generally comprises three separate stages:

- **PREPARATION**
- **DECOMPOSITION**
- **DETERMINATION**
Example  Typical Soil Sample Analysis

**Preparation**

- Dry and sieve to -80 mesh

**Decomposition**

- Weigh 0.5 g and digest in 10 mL of Aqua Regia

**Determination**

- Analyse solution for 30 elements by ICP-Emission Spectrometer
# How, What and Why of Assaying

## Analytical Process

**Objective:** Generate a sub-sample representative of the target phase or phases in the original sample.

<table>
<thead>
<tr>
<th>Drying:</th>
<th>Removes moisture allowing easier processing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Typically at 60°C to 90°C for most materials</td>
</tr>
<tr>
<td></td>
<td>Ambient drying (&lt;40°C) to preserve amorphous oxides</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sieving:</th>
<th>Used mainly on un-consolidated materials to extract the most active mineral phases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Soils and sediments to -177 microns (-80 mesh)</td>
</tr>
<tr>
<td></td>
<td>Till to -63 microns (-230 mesh)</td>
</tr>
<tr>
<td></td>
<td>Moss Mats screened for trapped sediments</td>
</tr>
<tr>
<td></td>
<td>Wet screening can extract down to clay-size minerals (-400 mesh)</td>
</tr>
</tbody>
</table>

**Caution:** Screening may remove the desired element

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Analytical Process

PREPARATION

-230 -150 -80 -20 +20
Mesh Mesh Mesh Mesh Mesh
Analytical Process

- **Crushing:** rock and drill core samples are crushed to produce a coarse fraction (REJECTS).
  - Industry standard is a jaw crusher capable of crushing down to 70 – 85% passing 10 mesh.
  - Jaw plates composed of a non-contaminating metal
  - Compressed air used to clean between samples and quartz used to clean between jobs or after mineralized samples.

- **Splitting:** generates a *non-biased* sub-sample from the crushed (REJECTS) fraction.
  - Riffle Splitter: a splitter with alternating slots to divide the sample by halves, narrower slots produce a more uniform split.
  - Rotary Splitter: has a carousel of triangular catching pans rotating beneath a vibratory fed stream of crushed material.
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Analytical Process
How, What and Why of Assaying

**Analytical Process**

**Pulverizing:** applied to crushed rock and drill core samples or any other material of reduced particle size (e.g., Heavy Mineral Concentrate) to produce a fine fraction (PULP) ready for analysis.

- Industry standard is to pulverize to 95% passing 150 mesh (100 microns).
- Ring and Puck Pulverizers are standard.
- Mild Steel (low-Cr) is preferable to minimize contamination. However, W-steel and Cr-steel pulverizers are common.
- Pulverizer bowls, rings and puck are cleaned by brush and compressed air between samples.
- Cleansing quartz wash used between jobs and between obviously mineralized samples.
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Analytical Process
Objective: To generate a uniform solution containing the analyte of interest that is readily analysed by instrumental or colorimetric methods.

TWO PRINCIPLE CATEGORIES

PARTIAL

- Partial Digestion (leach): attempts to extract the most labile phases of the elements or compounds of interest

TOTAL

- Total Decomposition: attempts to decompose all minerals present within the sample thereby liberating all of the element or compound of interest

DECOMPOSITION

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Analytical Process

Objective: To weigh a precise *aliquot* of the prepared sample into suitable labware in preparation for digestion.

WEIGHING

- Aliquots are generally weighed to within ±5% of the desired weight. The LIMS captures the weight and adjusts the concentration appropriately.

- Depending on the method of analysis samples may be as little as 0.1 g or as large as 1000 g.

*The relationship between the aliquot size, the particle size containing the analyte of interest and the rarity of the particles in the aliquot will be a major determining factor of accuracy and precision.*
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Analytical Process

WEIGHING

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Objective: To release the analyte of interest from the aliquot in a controlled manner into a stable solution.

DECOMPOSITION

- **PARTIAL DIGESTION**: Frequently referred to as leaches, partial digestions may be weak, moderate or strong in their attack. A Partial Digestion may be selective (attacking only one mineral substrate) or non-selective (attacking all mineral substrates).

- **TOTAL DECOMPOSITION**: As the name suggests, these methods decompose all of the sample (or nearly so). Decomposition may use hot, strong mineral acids (usually including hydrofluoric) or dry fluxes heated to a high temperature.
PARTIAL DIGESTION

Why choose a Partial Digestion?
Knowing the mode of occurrence of an analyte can provide information on the source and the means of transport. A partial digestion can increase the contrast between anomalous and background values.

Examples:
- Water is a weak and selective leach conducted at room T° to dissolve only water-soluble compounds like salts.
- Aqua Regia is a strong mineral acid (HCl + HNO₃) leach conducted at 95°C liberating elements in salts, exchange sites, carbonates, oxides, hydroxides, sulphides, etc. The leach is therefore non-selective.
PARTIAL DIGESTION

Aqua Regia being added to 0.5 g sample aliquots in test tubes before being added to a hot-water bath to improve digestion.
TOTAL DECOMPOSITION

• Why choose a Total Decomposition?
  Total decompositions report the absolute abundance of an element or compound within the sample.
  
Examples:
• 4-Acid Digestion uses nitric, perchloric and hydrofluoric acids heated until dryness to decompose most minerals (including silicates) to metal salts that are then back leached into either Aqua Regia or concentrated HCl.
  
• Fire Assay Fusion uses dry fluxes (PbO, silica, borax, etc.) heated at 1050°C to totally melt the sample and collect precious metals in the resulting liquid Pb metal. In the second stage, the Pb button is oxidized at 950°C and absorbed by a bone ash cupel to render a pure precious metal bead.
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TOTAL DECOMPOSITION

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Geochemical Analysis vs Assay

- Geochemical Analysis digestions are generally focused on trace to ultra-trace concentrations. Sample weights to acid volumes are a compromise between minimizing dilution and maximizing Total Dissolved Solids with the solution (e.g. 1g in 20 mL).

- Assay digestions are focused on moderate to high concentrations commonly found in mineralized samples. Volume of acid used to sample weight is several times higher than a geochemical digestion (e.g. 1g in 100 mL). In addition highly precise labware is used to ensure greater precision and accuracy in the analysis (e.g. Class A 100 mL volumetric flask).
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Geochemical Analysis vs Assay

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Analytical Process

Destructive vs Non-Destructive

- **Partial Digestions and Total Decompositions** rely on leaching or decomposing the sample to extract the element or compound of interest prior to determination. Because these methods require destroying the sample (to varying degrees), they are referred to as Destructive Analyses.

- **Non-Destructive Analyses** are analytical methods that do not require extracting the element or compound into a solution (i.e. no digestion) and are referred to as Non-Destructive Analyses (e.g. Neutron Activation Analysis, X-Ray Fluorescence)
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Objective: To measure the analyte concentration with an acceptable degree of precision and accuracy.

- Analytical instruments have undergone quantum leaps in the past 4 decades with respect to the sensitivity and suite of elements that can be determined simultaneously.

  1960’s & 70’s: Atomic Absorption Spectrometry
  1970’s & 80’s: ICP Optical Emission Spectrometry
  1990’s & 00’s: ICP Mass Spectrometry
Atomic Absorption Spectrometry

- Based on the absorption by atoms of a specific analyte of light emitted by a cathode lamp of the same analyte. A solution of the analyte is aspirated into an oxygen-acetylene flame operating at 3000°C in the direct path of the light beam. Pure solutions of known concentrations of the analyte are aspirated into the instrument to calibrate the results.

Pros: Very good accuracy and precision
      Fast and simple to operate

Cons: Prone to interferences by other elements
       Single element determination
       Limited dynamic range (two orders of magnitude)
How, What and Why of Assaying

Analytical Process

Atomic Absorption Spectrometry

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Analytical Process

ICP Optical Emission Spectrometry

- Based on emission of light of specific wavelengths onto a single or bank of CCD chips. Solutions aspirated into a plasma operating at 8000°C cause atoms to excite and emit light at characteristic wavelengths. Wavelength and intensity determines the analyte and its concentration. Pure solutions of known concentrations of the analytes are aspirated into the instrument to calibrate the results.

Pros:
- Very good accuracy and precision
- Simultaneous multi-element determination
- Large dynamic range (five orders of magnitude)

Cons:
- Prone to interferences by other elements
- Complicated to operate
How, What and Why of Assaying

Analytical Process

ICP Optical Emission Spectrometry
How, What and Why of Assaying

Analytical Process

ICP Mass Spectrometry

- Based on detection of atoms striking a target. Solutions aspirated into a plasma operating at 8000°C create charged ions. In a quadrupole mass spec the quadrupole establishes an EM field that only atoms with the correct mass and charge can travel through to strike the target. Pure solutions of known concentrations of the analytes are aspirated into the instrument to calibrate the results.

Pros:
- Good accuracy and precision
- Simultaneous multi-element determination
- Large dynamic range (seven orders of magnitude)

Cons:
- Prone to interferences by other elements
- Very complicated to operate
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Analytical Process

ICP Mass Spectrometry

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Analytical Process

**Neutron Activation Analysis**

- Based on measurement of gamma ray wavelengths indicative of each elements. Pulps are placed in plastic vials and exposed to the neutron flux in the heart of a nuclear reactor. After a brief cooling period, the wavelengths and intensities of gamma rays are measured by a gamma ray detector. Reference materials in the sample sequence to calibrate the results. A non-destructive, total analysis.

**Pros:**
- Good accuracy and precision for some elements
- Simultaneous multi-element determination
- Large dynamic range for some elements

**Cons:**
- Prone to interferences by other elements
- High detection limits for most base metals
- Requires a nuclear reactor

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Analytical Process

X-Ray Fluorescence

- Based on measurement of X-ray wavelengths indicative of each element. Pulps are irradiated by x-rays from a Mo or W cathode tube. Excited electrons are replaced by others returning to the ground state that emit x-rays. An x-ray detector measures wavelengths and intensities. Reference materials in the sample sequence calibrate the results. A non-destructive, total analysis.

Pros:
- Very good accuracy & precision for some elements
- Simultaneous multi-element determination
- Large dynamic range for some elements

Cons:
- Prone to interferences by other elements
- High detection limits for all elements
- Elements with masses < Ca are a problem

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Ensuring Quality

Quality Assurance / Quality Control

Quality Control: the monkey checking light bulbs at the end of the assembly line.

Quality Assurance: The planned production, testing and improving of a product or service.

What to look for?
Certification to an internationally recognized standard of quality.
ISO 9001:2000 or ISO 17025

A dynamic quality system overseen by a dedicated management-level staff member.

Reporting of quality control materials (lab duplicates, reference materials, blanks, etc.)
Ensuring Quality

Laboratory QC Materials

**Preparation Blanks:** Usually a lean material (quartz or granite) processed as the first sample in a job and carried through all stages of analysis. Gives background contamination at all stages. (Method Detection Limit).

**Reagent Blanks:** Aliquot of acid solution or flux digested and analysed with samples. Gives background for reagents, digestion process and instrument (Detection Limit).

**Preparation Duplicate:** a second split of the crushed fraction that is prepared, weighed, digested and analysed with its duplicate mate. Measures method reproducibility (Method Precision).

**Pulp Duplicate:** a second split of a pulp sample digested and analysed with its mate (Precision).
Reference Materials: a solid or liquid of known or established concentration and having (more or less) the same matrix as the samples being tested and analysed with the samples. (Accuracy)

- Materials may be internationally certified (CRM) or internally certified (In-house Reference Material).
- Concentrations are reported as Recommended (with a statistical degree of certainty) or as Informational.
- Care should be taken to ensure that reference materials match the needs of the samples to be analysed.
- Great care should be taken to ensure that the method of analysis used in certifying the RM is compatible with the current test method.
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Ensuring Quality

Reference Materials

Control Charts: is the most common graphical method of evaluating the quality performance of an analytical method.

Group 1F-MS Standard DS4 - Cs

Concentration (ppm)

Insertions
Ensuring Quality

General Standards of Quality

- **Weak Leaches**: (Water, ammonium acetate, MMI)
  - Precision of ±30% or better
- **Strong Partial Digestions**: (Aqua Regia)
  - Precision of ±10% or better
- **Total Decompositions**: (Lithium metaborate fusion)
  - Accuracy and Precision of ±5% or better
- **Assay Analysis**: (Ore-grade)
  - Accuracy and Precision of ±3% or better

But in addition look for...
- Good Turnaround
- Good Service
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LIMS

Network of all hardware and software that controls the flow of work and information both within and exterior to the lab.

General Features:
- Maintains all client information and preferences
- Tracks all samples within and between laboratories
- Identification of all work in all analytical process stages
- Controls and sequences the analytical processes
- Integrates with automated instruments and evaluates data integrity
- Provides short and long term QC evaluation
- Generates data output and invoicing
- Provides client access to work status and data download via a web interface
- Provides audit trail of all work or re-work done
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“...every time I get new data, occasionally there’ll be a Maurice Richard hockey sweater but most often its Aunt Betsy’s knitted socks” JG

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Your Survey

Before Starting

- **Determine the focus of your survey:** Searching for a commodity or a prospective rock unit
- **Research known databases:** Is it necessary to re-create the wheel?
- **Scale:** How large of a survey area to explore and what density of sampling to use?
- **Budget:** What is the best compromise between cost and sampling density?
- **Select the Appropriate Test Method:** What is the best compromise between budget and test method?
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Your Survey

Recreating the Wheel?

With analytical detection limit of 5 ppb

With analytical detection limit of 0.2 ppb

St. Andre de Restigouche – Geologie Quebec – Marc Beaumier, 2002

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Your Survey

When Starting

• Contact the Laboratory:
  If possible... by all means visit the laboratory
  Get a price quote for the test method based on the expected number of samples to be collected.
  Ask what the turnaround time is currently and what it will be during the peak season

• Acquire Reference Materials:
  National Instrument 43-101 places the responsibility for the quality of all work conducted on an exploration program with the Qualified Person... including verifying the quality of work conducted by the lab
Your Survey

WhenSubmittingSamples

- **Properly Label and Package your samples**: Samples should be dried before shipping and uniquely labeled on two spots or two modes (e.g. permanent marker on the sample container and sample tag in the container with the sample). Include a sample submission form with client information (name, address, etc.), who to invoice, who will receive the data, test method required, a list of samples (if possible) and disposition of all materials after completion of analysis.

- Use a robust shipping container that is properly labeled with client information and sample sequence contained inside.

- **When shipping samples**: Notify the lab that samples have been shipped, shipping details and priority (if any) for their analysis.
How, What and Why of Assaying

Your Survey

How Not to Ship Samples
How, What and Why of Assaying

Your Survey

Good Luck!