ANALYTICAL ASPECTS OF BIOGEOCHEMISTRY

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LabWest Background

- Established in 2009, a boutique laboratory service
- Small team focus
  - We have more than 90 years team experience in mineral exploration analysis
- Developed and specialised microwave assisted digestion techniques for low level analysis

Key Staff

- Brad Whisson, Managing Director
- Andrew Daly, Laboratory Manager
- Mary Trutwein, Client Services and Quality System Manager
- Dr Shaun Height, Operations Manager




We are the people who actually answer the phones

Biogeochemistry Analysis is Complex

- Key element markers are present at low concentration in the sample
- Some elements that may be targets can be part of the plants system, complicating interpretation.
- Contamination is a critical concern due to the low levels involved
- Partner with an expert dedicated laboratory important for value and success

Collecting samples

- On-site preparations
  - Pre-drying, prevents samples from rotting
  - Preservation
  - Loss of moisture
    - Low transport weight = Low transport cost
- Packaging for transport
  - Contamination from road dust
  - Sample security – loss of integrity
  - Quarantine

Quarantine


QUARANTINE AREA
NO ENTRY OR REMOVAL OF GOODS
AUTHORISED PERSONS ONLY
HEAVY PENALTIES APPLY
QUARANTINE ACT 1908
NO ENTRY
AUTHORISED PERSONNEL ONLY
MICROBIOLOGICAL CONTAINMENT
QC1 FACILITY
EYE PROTECTION MUST BE WORN BEYOND THIS POINT

Quarantine

- Australian International Quarantine
  - Requires an Import Permit ($200 - $300) and can take 3-4 weeks to process. Need species identification.
  - Samples will need to be treated before they can be released from quarantine.
  - Treatment method gamma irradiation 25kGy
  - Typical process is to send the samples directly to the treatment facility e.g. SteriTech, they will process and then forward to the laboratory.
  - This can take some time! Small shipments might only be processed weekly or fortnightly.

Western Australia Quarantine

- WA has a separate Quarantine Act, *Biosecurity and Agriculture Management Act 2007 (BAM)*
- WA is free of many pests, weeds and diseases that are present elsewhere in Australia
- Plants and plant products must be declared and inspected on entry.

Western Australia Quarantine

- Check on WA Organism List the status of the plant being imported.
  https://www.agric.wa.gov.au/bam/western-australian-organism-list-waol
- A permit may be required. Also could take 4 weeks!
  - Permitted (S11) e.g. Spinifex from QLD or Mitchell Grass from NT
  - Permitted with a permit (R73), e.g. Myrtacae family are restricted – SW Eucalypts are free from Myrtle Rust
  - Prohibited (S12)

Preparation Procedures

On receipt at the lab.

Do samples need to be washed?

- Maybe? Best to decide on a case by case status.
- Collecting from area of previous high drilling or other human activity – could be contaminated by drilling dust so a wash might be warranted.
- Collecting from virgin area, may not be required.

Washing Procedures

- Rinse in a bucket or tub

- Ultrasonic bath

Washing medium

- Tap water – can contaminate Ca, Mg, Cu
- Distilled water or RO water

- Detergents – can contaminate S, P, K, Si

- Ionic surfactants e.g. Triton X

- Methylated spirits, ethanol, isopropanol

Drying

- Drying temperatures
  - 40°C - 80°C drying temperature range
  - 24 hours at 60°C is the typical drying protocol
    - arid area plants (xerophytes) are very good at holding onto moisture so may require an extended time

Sampling

- In general, We will prepare entire sample as it is received unless otherwise directed.
  - Remove foreign matter – windblown, dead twigs.
  - Only prepare leaves or foliage, remove stem or bark.
- Consistency is key.

Preparation Methods

- Type of machine used depends on a couple of factors
  - Size and shape of the sample
    - Can you prepare the whole sample or a staged preparation?
  - Is a particular contamination an issue

Preparation Methods

- Knife Mill – Retsch GM300
  - Stainless steel blades

Spinifex prepared in GM300

Preparation Methods

- Blender style
  - Stainless steel blades

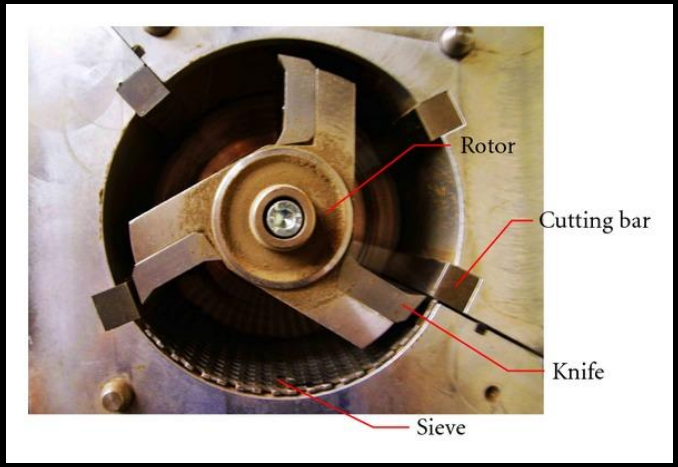
Other Preparation Methods for smaller samples

- Coffee or spice grinder

- Mortar and pestle

Other Preparation Methods

- Hammer type cutting mill
  - Metal cutting parts



- Ring or Puck Mill
  - Metal parts or agate head

- Disc grinder

Other Preparation Methods

- Cryogenic grinding
  - Expensive
  - Sample size limited
  - Need a staged preparation

- Jet Milling
  - Quite Expensive
  - Need a staged preparation

Contamination

- Blades – Stainless Steel Ni, Cr, Fe
  - Sample hardness does play a role
  - Varies by sample type, spinifex is very hard
- Bowls – Al or plastic
- Essential Oils – oil release builds up gum
  - Wash equipment between samples, methylated spirits, acetone

Analysis Methods

- Neutron Activation Analysis – direct analysis
- Sample Digestion with Instrumental Analysis of the solution
  - Ash First then Acid Digestion
  - Direct Acid Digestion
  - Direct Acid Digestion using Microwave
- Fusion Analysis

Neutron Activation

- Sample irradiated in a nuclear reactor to create artificial radioactive isotopes of all the elements.
- Artificial Radioactive isotopes then decay by gamma radiation which is characteristic of the elements in the sample

Neutron Activation Pros and Cons

- Pros
  - No or minor sample preparation required
  - Considered to be a true bulk composition analysis
- Cons
  - Not really available in Australia
  - Expensive

Ash First Acid Digestion

- Typically 20-25g sample heated 470°C for 12 - 16 hours. Removes all organic carbon.
- Digestion of residue with either Aqua Regia or Nitric acid followed by instrumental reading of the solution.

Ash First Acid Digestion Pros & Cons

- Pros
  - Removes the bulk of the plant matrix
  - Concentrates low level trace elements usually by a factor of 20 to 30.
- Cons
  - Loss of some volatile elements
  - Different plants can also be influenced by the burn temperature – more or less ash. Maybe important to consider if submitting varieties of plants.
  - Low sample residue means it can easily be contaminated by the equipment used or from other types of samples.

    e.g. labs will use same furnaces for different tasks.
  - Expense

Direct Acid Digestion

- Typically a similar procedure as applied to soils or rock chip samples.
- 0.5 – 1g samples weighed into test tube and treated with aqua regia or nitric acid.
- Heated at 100 – 120°C for 1-2 hours on a hotplate or in a hotbox.
- Instrumental Analysis of solution

Direct Acid Digestion Pros & Cons

- Pros
  - Simple process, very easy to do large sample numbers
  - Low Cost
- Cons
  - No concentration effect
  - Very low extraction efficiency
  - Temperature is limited by boiling point of acids used.
  - Partial digestion of the sample
  - Loss of volatile elements e.g. Ge
  - Easy cross contamination

Our Background using Microwave Digestions

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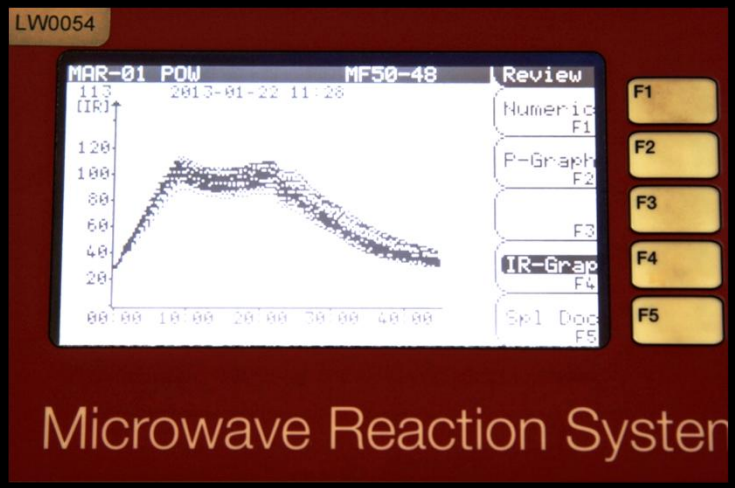
Microwave technology adopted early

- > 400,000 mineral analyses using microwave systems.
- Wide range of sample types handled.
  - Soils
  - Lags
  - Rock Chips
  - Minerals
  - Methods developed and validated.

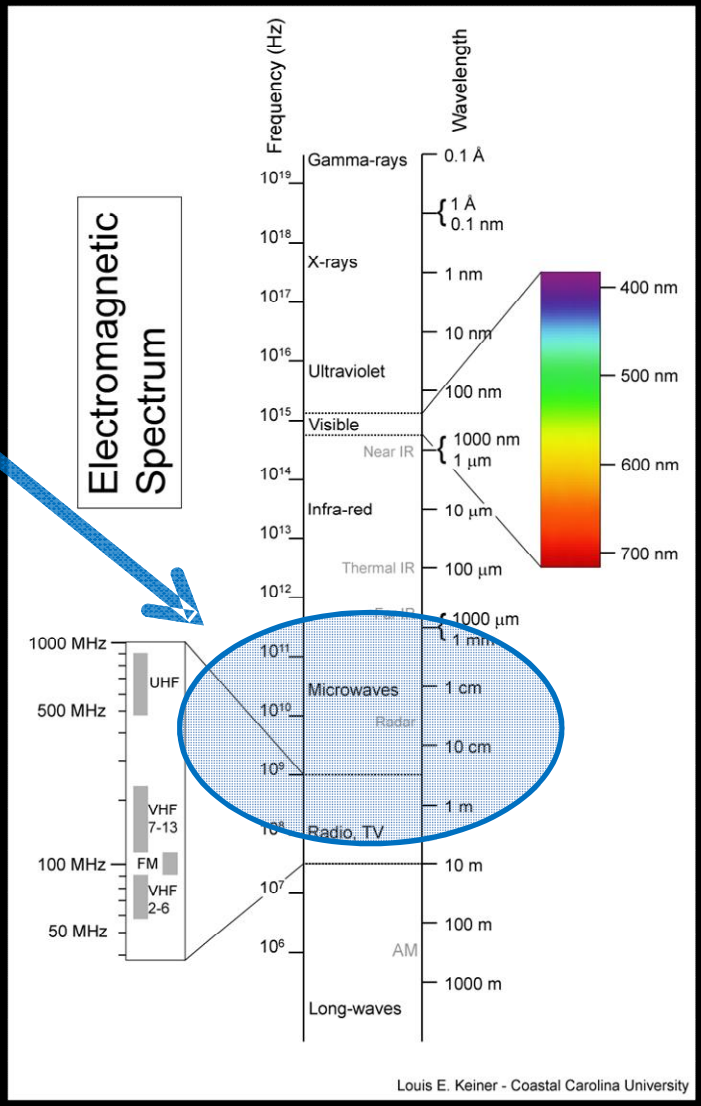


About Microwave Digestions

Microwaves:
ν= 300MHz – 300GHz
(λ = 1mm – 1m)

- Rapid energising of molecules

- Laboratory instrument features
  - 1400W output
  - Corrosion Resistant
  - Sealed pressure vessels (~ 20 – 80 bar)
  - Pressure and Temperature control
  - Recording of parameters
  - Multiple safety measures



Technical Advantages

- Digestion time: 0.5 – 1 hour
- High P and T
  - 160°C - 200°C, 20 - 80 bar
  - Not limited to b.p. of acids (HF ~104°C)
  - Acids are more oxidising at high temp, therefore dissociate matrices very effectively.
- Sealed vessel:
  - More efficient use of acids
  - Environmental advantages
  - Sealed vessel retains volatiles
- Reproducible digestion conditions

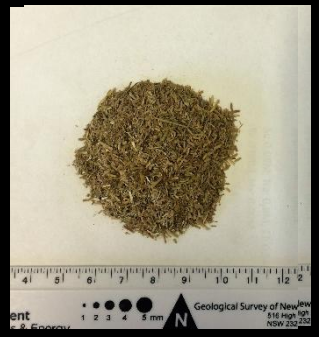
Microwave Direct Acid Digestion

- 0.5 – 2g samples weighed into microwave test tube and treated with aqua regia or nitric acid.
- Heated at 160 - 200°C for 20 minutes in a microwave under very high pressure 80 Bar (8000 kPa or 1160 psi)
- Instrumental Analysis of solution

Variation in 2g weighed samples

Spinifex
Region: QLD

Spinifex
Region: NW WA



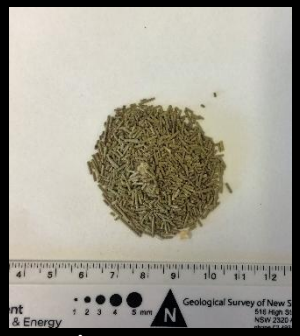
Spinifex
Region: NW WA

Spinifex
Region: NW WA

Mitchell Grass
Region: NT

Eucalyptus
Region: Australia

Eucalyptus
Region: East WA



Mulga
Region: Central WA

Desert Pea
Region: NW WA

Buffalo Grass
Region: My front lawn

Incidentally,

2g Spinifex

20g Spinifex

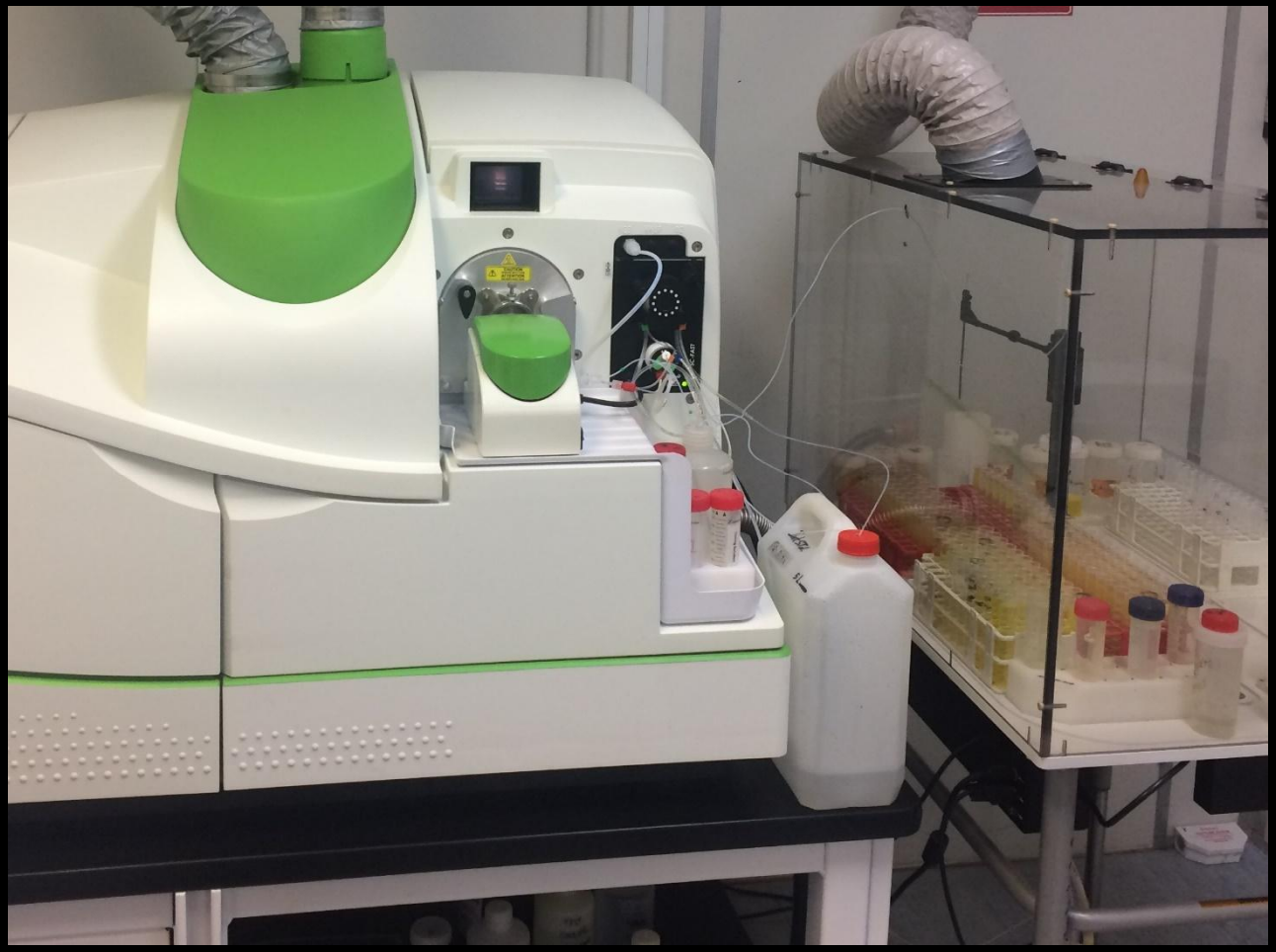
Microwave Direct Acid Digestion Pros & Cons

- Pros
  - Simple process
  - Consistent, reliable, efficient digestion
  - Comparable extraction to ash method without any contamination issues
  - No loss of any volatile elements
- Cons
  - Maximum of 2g sample analysis with current technology
  - No concentration effect, but this is offset by the use of ICPMS

Instrumental Analysis

- ICPMS – Inductively Coupled Plasma Mass Spectrometry
- ICPOES – Inductively Coupled Plasma Optical Emission Spectrophotometry

ICPMS – ICP Mass Spectrometry



Perkin Elmer NEXION 300 at LabWest

ICPOES – ICP Optical Emission Spectrophotometry

Perkin Elmer OPTIMA 7300 at LabWest

Quality Assurance Within the Laboratory

- Quality System
- ISO9001:2005
- NATA Accreditation

Reference Materials

- Certified Reference Material Suppliers
  - NIST
  - NCS
  - Swan Leaf

Reference Materials

- In-house Reference Materials
  - Spinifex
  - Mulga
  - Spiked Buffalo Grass
  - Africa Box Hedge

Batch Controls

- Reagent Blanks
- Duplicate samples (splits)
- Replicates
- Instrument Control Solutions

Batching effects – Can they be real and how would you avoid them.

- Labs split samples into batches for processing.
- Batch effects can be from baseline shifts, changes in calibration and conditions.

- Good lab QC should eliminate any batching effects.
- Run all samples in a single instrument run.

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Questions?

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