MAT 252 Mass Spectrometer
### Mass Spectrometer Types: Many Analytical Purposes

**Analyzer**

**Source**

**Collector**

**Source:** (Ionize, accelerate, collimate)

<table>
<thead>
<tr>
<th>Usual Types:</th>
<th>Gas</th>
<th>TIMS</th>
<th>Thermal Ionization Mass Spec; heated filament</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Types:</td>
<td>SIMS</td>
<td>Resonance Ion Mass Spectrometer- Selective ionization w/ laser</td>
<td></td>
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<tr>
<td></td>
<td>RIMS</td>
<td>Inductively-Coupled Plasma Mass Spectrometer</td>
<td>ionize nearly everything, great for trace elements</td>
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<tr>
<td></td>
<td>ICPMS</td>
<td>Accelerator Mass Spectrometry</td>
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<td></td>
<td></td>
<td>AMS</td>
<td>High energy, <em>e.g.</em> 6 MeV generated by tandem accelerator.</td>
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<tr>
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<td>Extremely high sensitivity- few 1000's atoms/mg sample</td>
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</table>
Double-Focusing Mass Spectrometer

A.O. Nier (1989)
Mars Atmosphere @ 135 km
Viking Lander, 1976

A.O. Nier (1989)
RIMS  Resonance Ionization Mass Spectrometry

Selectively ionize atoms with narrow band laser or beam that is specifically tuned to match the energy level spacing for the desired element.

High sensitivity permits analysis of elements present in ppm or even ppt quantities

Ionization efficiency of the selected element can be as much as $10^9$ x greater than for another element.

**LARIS** = Laser Atomization RIS  Ionize sample with laser

**SIRIS** = Sputter Initiated RIS  Ionize sample with ion beam
**SIMS** (Secondary Ion Mass Spectrometry) = ion probe

Secondary ions are produced by ion bombardment of a sample.

Utilizes double focusing mass spectrometer to get high mass resolving power (MRP), w/o large loss of transmission, needed to eliminate isobaric interferences (esp. hydrides).

Very high sensitivity (< 1 ppb);
   Can use *very* small samples, to 1 femtogram, or $10^{-15}$ g.

Very good for trace element measurements & for small-scale isotopic variations
SHRIMP ANALYZER
ION OPTICS

MAGNET
QUADRUPOLE LENS
ENERGY SLIT
ENERGY ANALYZER
BEAM \(\alpha\)-LIMITER
SOURCE SLIT
SAMPLE
VACUUM LOCK
PUMP
PUMP
PUMP
ION MULTIPLIER
FARADAY CUP
COLLECTOR SLIT
FIELD CLAMPS
PRIMARY ION SOURCE
ION OPTICS

Eldridge et al. (1989)
Mass 48: Cameca IMS 3f Ion Microprobe

\[
\text{MRP} = \frac{m}{\Delta m} = \frac{48}{0.0045} = 10,700
\]
Cameca NanoSIMS 5.0

- High spatial resolution (smaller primary beam)
- High sensitivity at High Mass Resolution
- Multi-detection
- Allows for isotopic analysis of submicron samples
Accelerator Mass Spectrometry (AMS)

Uses accelerators to measure isotopic abundances and concentrations of elements at very high sensitivity levels.

Accelerator, located between ion source and detector, is used to separate isobars or to dissociate interfering molecular ions, or both.

Application to "long-lived" cosmogenic radionuclides ($T_{1/2} = 0.1$ to $16$ Ma)

- $^{10}$Be ($1.5$ Ma)
- $^{26}$Al ($0.72$ Ma)
- $^{36}$Cl ($0.30$ Ma)
- $^{129}$I ($16$ Ma).

No primordial concentrations remain, but these are continually produced by:

- Cosmic rays hitting the atmospheric,
- Cosmic rays hitting rocks and extraterrestrial materials
- Nuclear bombs

All have half lives too long to be measured by counting of decay events.

Ultrahigh sensitivity- isotope ratios down to $10^{-15} = \text{few thousand atoms/mg sample!}$

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{10}$Be</td>
<td>Sediment subduction</td>
</tr>
<tr>
<td>$^{10}$Be, $^{36}$Cl, $^{26}$Al</td>
<td>Erosion rates</td>
</tr>
<tr>
<td>$^{36}$Cl, $^{129}$I</td>
<td>Groundwater hydrology</td>
</tr>
<tr>
<td>$^{14}$C, $^{10}$Be, $^{26}$Al, $^{36}$Cl, $^{129}$I</td>
<td>Solar variability</td>
</tr>
<tr>
<td>$^{14}$C, $^{10}$Be, $^{26}$Al, $^{41}$Ca, $^{36}$Cl, $^{129}$I</td>
<td>Meteorites (exposure age; terrestrial age)</td>
</tr>
<tr>
<td>$^{14}$C</td>
<td>Dating of extremely small samples</td>
</tr>
</tbody>
</table>
NOTATION, STANDARDS, & ISOTOPIC MIXING

FUNDAMENTAL DEFINITION:

Isotope Ratio: \( R = \frac{\text{moles isotope 1}}{\text{moles isotope 2}} \)

\( = \frac{\text{D/H}}{\frac{13C}{12C}} \frac{18O}{16O} \text{ etc.} \)

Caution: Alternate R's are often useful, but not exactly the same

1) \( R = \text{mass isotope/total mass element} \)
2) \( R = \text{moles isotope/total moles element; can approximate true R for trace heavy isotope} \)

For some ratios involving radiogenic isotopes, R is sensible unit for reporting data

\( e.g. \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \sim 0.7032 \text{ to } > 0.7100 \text{ in modern igneous rocks } \) (large variations)

\( R \) is useful for mathematical derivations

\( R \) is generally not useful for reporting stable isotope data because:

1) Heavy isotope abundances are very low \( \frac{\text{D/H}}{0.000156}; \frac{18O}{16O} \sim 0.002005 \)
2) Natural variations too small
3) Hard to make precise measurements of absolute abundances
Delta Values

Abundance variations of stable nonradiogenic isotopes are normally small.

A difference technique (formerly, voltage divider) is used to compare the mass spectrometer beam intensities with those of a standard gas.

It is natural and best to report the isotopic constitution of a sample \((x)\) in terms of its *dimensionless difference* from a known standard \((\text{std})\).

Define the \(\delta\)-value ("delta-value"):

\[
\delta = 1000 \frac{R_x - R_{\text{std}}}{R_{\text{std}}}
\]

where R's are isotope ratios

1000x converts the \(\delta\)-values to per mil \(\‰\)

Some workers use 100x and \% for D/H

\[
\delta^D = 1000 \frac{(D/H)_x - (D/H)_{\text{std}}}{(D/H)_{\text{std}}}
\]

\[
\delta^{18}O = 1000 \frac{(^{18}O/^{16}O)_x - (^{18}O/^{16}O)_{\text{std}}}{(^{18}O/^{16}O)_{\text{std}}}
\]
\[ V = iR \]

Equalize voltages

\[ \frac{i_{45}}{i_{44}} = \frac{R_{44}}{R_{45}} \]
**Delta Values**

Abundance variations of stable nonradiogenic isotopes are normally small.

A difference technique (formerly, voltage divider) is used to compare the mass spectrometer beam intensities with those of a standard gas.

It is natural and best to report the isotopic constitution of a sample (x) in terms of its *dimensionless difference* from a known standard (std).

Define the **δ-value** ("delta-value"):

\[
\delta = 1000 \frac{R_x - R_{std}}{R_{std}}
\]

where R's are isotope ratios

1000x converts the δ-values to per mil ‰

Some workers use 100x and % for D/H

\[
\delta^{18}O = 1000 \frac{\left(\frac{^{18}O}{^{16}O}\right)_x - \left(\frac{^{18}O}{^{16}O}\right)_{std}}{\left(\frac{^{18}O}{^{16}O}\right)_{std}}
\]

\[
\delta^{18}O = 1000 \frac{\left(\frac{^{18}O}{^{16}O}\right)_x - \left(\frac{^{18}O}{^{16}O}\right)_{std}}{\left(\frac{^{18}O}{^{16}O}\right)_{std}}
\]
ISOTOPIC STANDARDS: Chosen for convenience

O and H isotopes:
SMOW Standard Mean Ocean Water Craig (1961)
\[ ^{18}O = 1989.5 \pm 2.5 \text{ ppm} \]
\[ D = 158 \pm 2 \text{ ppm} \implies D/H = 1/6328 \]

\[ ^{18}O = 2005.2 \pm 0.45 \times 10^{-6} \text{ (see O'Neil, 1986)} \]
\[ D = 155.7 \pm 0.1 \times 10^{-6} \implies D/H = 1/6422 \]

C (\&O) isotopes:
PDB Cretaceous belemnite from the Peedee Formation, NC
Craig, 1957; Friedman and O'Neil, 1977
Poor standard?
Inhomogeneous (e.g., seasonal variations)
All gone

S isotopes: Canyon Diablo troilite

N isotopes: Air
Isotopic Fractionation Factor

\[ \alpha_{A-B} = \frac{R_A}{R_B} \]

Describes the partitioning of isotopes between two phases, A and B, produced by equilibrium or kinetic processes or some combination.

Typically, \( \alpha \sim 1.001 \) to 1.040 except for D/ H in certain cases

Sometimes used: \( \varepsilon = 1000(\alpha - 1) \)

Confusion with different epsilon units used in Nd isotope studies
Relation between $\alpha$ and $\delta$

$$\alpha_{A-B} = \frac{1000 + \delta_A}{1000 + \delta_B}$$

*where* $\delta_A$ and $\delta_B$ must be reported relative to the same isotopic standard

**Important & exact relation**

Use to calculate the apparent or measured fractionation factor from the $\delta$-values of two associated phases

Use to predict the $\delta$-value of one phase from that of another if the fractionation factor $\alpha$ is known.
"BIG DELTA"

\[
\Delta_{A-B} \equiv \delta_A - \delta_B
\]

**Big Delta** provides a convenient but rough estimate of the "fractionation" between the two phases.

*e.g.*

\[
\begin{align*}
\delta_A &= +15.0 \permil \\
\delta_B &= -5.0 \permil \\
\Delta_{A-B} &= 20.0 \permil
\end{align*}
\]

A geochemist would state that "there is a 20 per mil fractionation between phases A and B", but the actual value of \( \alpha_{A-B} \) would be close to 1.0201
Exact

\[ \alpha_{A-B} = \frac{1000 + \delta_A}{1000 + \delta_B} \]

\[ \alpha - 1 = \frac{1000 + \delta_A}{1000 + \delta_B} - \frac{1000 + \delta_B}{1000 + \delta_B} = \frac{\delta_A - \delta_B}{1000 + \delta_B} \]

Approximations

\[ 1000(\alpha - 1) \cong \delta_A - \delta_B \]

\[ 1000 \ln \alpha \cong \delta_A - \delta_B \]

\[ \Delta_{A-B} \equiv \delta_A - \delta_B \cong 1000 \ln \alpha \cong 1000(\alpha - 1) \]
It is commonly necessary to convert the $\delta$-value of a sample ("X") measured relative to one isotopic standard ("S1") to that which would be measured relative to another ("S2").

This conversion is approximately made by adding the per mil difference, $\delta_{S2S1}$, between the two standards, but for an exact conversion use:

$$\delta_{S2}X = \delta_{S1}X + \delta_{S2S1} + \frac{1}{1000} (\delta_{S1}X) (\delta_{S2S1})$$

$e.g.$

$$\left(\delta^{18}O_x\right)_{SMOW} = 1.03086 \left(\delta^{18}O_x\right)_{PDB} + 30.86$$
after Friedman & O’Neil (1977)
Bob Method for STANDARD CONVERSION

\[ \beta = \frac{1000 + \delta X_{\text{Std1}}}{1000 + \delta X_{\text{Std2}}} \]

where

\[ \beta = \frac{R_{\text{Std1}}}{R_{\text{Std2}}} \]

e.g.

\[ 1.03086 = \frac{1000 + \delta X_{\text{SMOW}}}{1000 + \delta X_{\text{PDB}}} \]
Material Balance Relationships

Bulk isotope ratio of a multi-component system:

\[ R_{\text{system}} = \frac{\sum_{j=1}^{n} N_j^*}{\sum_{j=1}^{n} N_j} \]
\[ R_{\text{system}} = \frac{\sum_{j=1}^{n} N_j^*}{\sum_{j=1}^{n} N_j} = \frac{N_1^* + N_2^* + \ldots + N_n^*}{\sum_{j=1}^{n} N_j} \]

\[ R_{\text{system}} = \frac{N_1}{\sum_{j=1}^{n} N_j} \left( \frac{N_1^*}{N_1} \right) + \frac{N_2}{\sum_{j=1}^{n} N_j} \left( \frac{N_2^*}{N_2} \right) + \ldots \]

\[ R_{\text{system}} = \sum_{j=1}^{n} X_j R_j \]

where the \( X_i \) are the mole fractions of the reference nuclide of interest, such that:

\[ \sum_{j=1}^{n} X_j = 1 \]
Simple Binary Mixing

\[ \frac{(R_1 + R_2)}{2} \]
For a trace isotope of a minor element, the mole fractions $X_i$ are:

$$X_k = \frac{C_k M_k}{\sum_{j=1}^{n} C_j M_j}$$

For binary mixing:

$$\left[ \frac{(C_B)}{(C_A)} \left( \frac{R_{Mix}^+ - R_B^+}{R_{Mix}^+ - R_A^+} \right) \right]_{Element\ L} = \left[ \frac{(C_B)}{(C_A)} \left( \frac{R_{Mix}^+ - R_B^+}{R_{Mix}^+ - R_A^+} \right) \right]_{Element\ M} = \ldots = -\frac{\text{Mass\ A}}{\text{Mass\ B}}$$

where

$$R^+ = \frac{\text{mass\ of\ isotope}}{\text{total\ mass\ of\ element}}$$

Very nearly, $R = R^+$ for H, C and O isotopic systems.
end