

## Lecture 14 Measurements II: Mass spectrometry

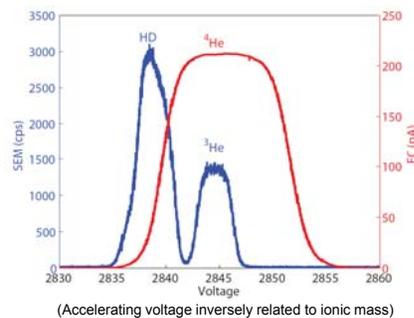
- Limits to detection/measurement
- Gas source mass spectrometry
- AMS
- Standardization
- Abundance measurements
- Isotopomeric interference
- Measuring half-lives

## Limits to Detection/Measurement

- Ionization is fundamentally a **Probabilistic Process**
  - Just like radioactive decay
  - So is transmission through the analyzer
- There is an intrinsic statistical uncertainty
  - Proportional to the number of counts<sup>1/2</sup> in an interval
  - Just like radioactive decay

## An example: helium isotopes

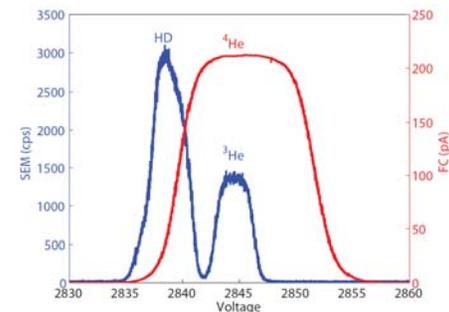
- Made on a statically operated dual-collecting gas source mass spectrometer
  - <sup>4</sup>He on Faraday cup
  - <sup>3</sup>He by ion counting (using SEM)
- “Fuzz” on <sup>4</sup>He due to ion source stability/electrometer noise
- Fuzz on <sup>3</sup>He due to ion counting statistics



<sup>3</sup>He count interval is 1 second  
~1400 counts/interval  
Intrinsic uncertainty ~ 2-3%

## An example: helium isotopes

- You are limited by the number of ions you count in the sample
- A typical experiment: count for ~ 1000 seconds
  - Total counts ~ 10<sup>6</sup> → Typical uncertainty ~0.1%



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## Gas Source Mass Spectrometers

- Dynamic vs. static mode of operation
  - Dynamic (mass spec pumped continuously)
    - Matched/calibrated dual viscous leaks\*
    - Larger sample requirement
    - Rapid cycling between standard & unknown
    - Very precise: e.g., stable oxygen, carbon, nitrogen, & sulfur isotopes
  - Static
    - Introduction into vacuum envelope (arrested pumping)
    - Smaller samples, more sensitivity
      - For ion counting limitations
      - Matrix and pressure effects

\*hopefully non isotopically fractionating

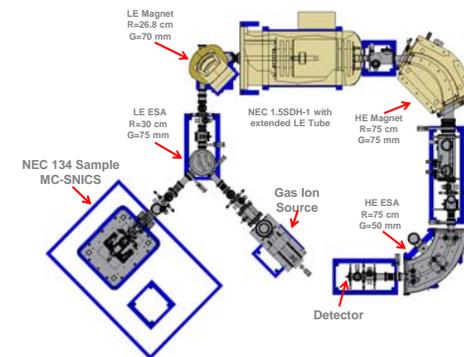
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## Accelerator Mass Spectrometry

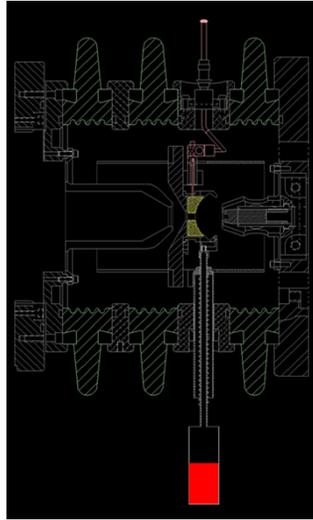
Where isotopic ratios are extraordinarily small, high voltage and many “filters” are required to separate isotopes. E.g.,  $^{14}\text{C}$ ,  $^{10}\text{Be}$ ,  $^{129}\text{I}$

Negative C ions  
created off graphite  
targets from 8 KV  
Cs beam (no -N)



## Cesium Sputter Ion Source

Need **Negative C** ions created off graphite targets from 8 KV Cs beam (no negative N ions): sputter beam creates heat/plasma at pressed target (mixture of Fe and C) interface



## Accelerator Mass Spectrometry

**Negative C** ions created off graphite targets from 8 KV Cs beam (no N)

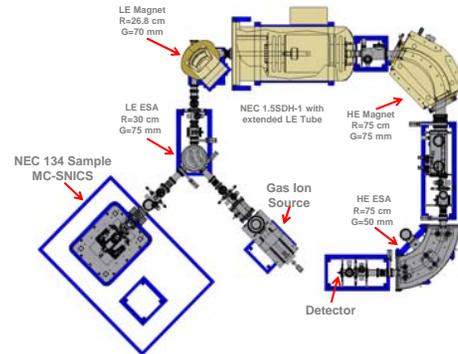
Most non-C ions eliminated in 60 KV bending magnet (sequential injector operating at 10 Hz)

<sup>-</sup>C accelerated to 0.5 MV

E-stripping in Ar produces <sup>+</sup>1C

Accelerated through 0.5 MV to ground

Where isotopic ratios are extraordinarily small, high voltage and many "filters" are required to separate isotopes. E.g., <sup>14</sup>C, <sup>10</sup>Be, <sup>129</sup>I



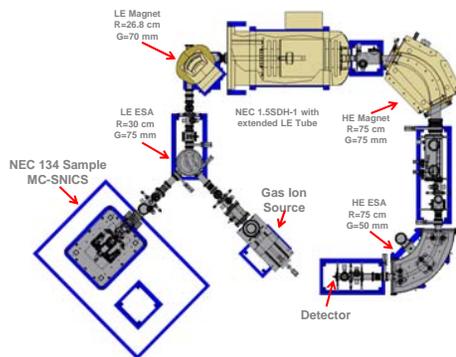
## Accelerator Mass Spectrometry

<sup>12</sup>C and <sup>13</sup>C separated off into faraday cups using a magnet

Additional electric and magnetic sectors to select against scattered ions

Detected in gas ionization detector (additional discrimination) or solid state detector

Where isotopic ratios are extraordinarily small, high voltage and many "filters" are required to separate isotopes. E.g., <sup>14</sup>C, <sup>10</sup>Be, <sup>129</sup>I

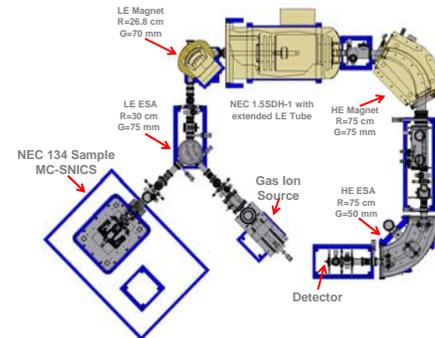


## Accelerator Mass Spectrometry

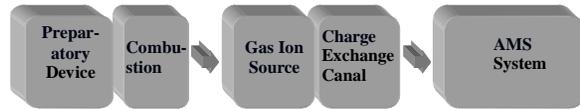
Where isotopic ratios are extraordinarily small, high voltage and many "filters" are required to separate isotopes. E.g., radiocarbon

The future:

Using a gas source (microwave plasma) for Continuous Flow AMS (CFAMS) & interfacing to GCs, etc for single compound analysis, or progressive reaction monitoring.



## Why CFAMS?



- Direct interfacing or injection attractive:
  - “real time” feedback
  - fewer steps (lower blank?)
  - Quicker turnaround
  - lower cost per analysis
  - less intrinsic memory than “hybrid” sources

## Gas Ion Source Performance

- **Gas Ion Source:** → Efficiency= 5.4%
  - 300  $\mu\text{l}/\text{min} = 1.4 \cdot 10^{17}$  C atoms/s
  - 1200  $\mu\text{A C}^+ = 7.6 \cdot 10^{15}$  C ions/s
- **Mg Charge Exchange Canal:** → Efficiency= 15%
  - 400  $\mu\text{A C}^+ = 2.5 \cdot 10^{15}$  C ions/s
  - 63  $\mu\text{A C}^- = 3.8 \cdot 10^{14}$  C ions/s
- **Total:** → Efficiency= 0.3-0.8%
- **Emittance, and Energy Spread**
  - ~70  $\pi \cdot \text{mm} \cdot \text{mrad}$  at 30 kV Extraction ( $\text{C}^+$  ions)
  - ~80-140  $\pi \cdot \text{mm} \cdot \text{mrad}$  at 30 kV Extraction ( $\text{C}^-$  ions)
  - $\pm 320$  eV beam energy spread at 30 kV Extraction

Compare with a modern sputter source: Ion Source efficiency ~ 25%  
emittance ~ 40  $\pi \cdot \text{mm} \cdot \text{mrad}$  at 60 kV

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## Instrument Standardization is Critical

- Mass spectrometers are “ratiometric” instruments
  - Because many processes (esp. ionization) is parametric (depends on unknown factors)
- Standards must be
  - Uniform
  - Readily available
  - Relevant (for a specific problem)

## Standard choice is related to problem

- For example:
  - Oxygen isotopes: PDB vs SMOW vs atmospheric oxygen
  - Must convert between reference standards
    - Beware of delta notation: just because a standard is 44‰ different you don't subtract 44‰ (you divide by 1.044 !)
  - Sulfur isotopes: Canyon Diablo Troilite
    - Gotcha! Started with SO<sub>2</sub> methodologies (poor precision), but SF<sub>6</sub> methods showed it was heterogeneous.

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## Peak Height Manometry

- Assume instrument has linear\* response as a function of sample size
  - Assumes reproducible, unbiased delivery to instrument
    - Fraught with challenges if not quantitative
  - First order dependence on yield and instrument sensitivity changes
    - Limited by electronics, vacuum quality, etc. to about 0.1-1%

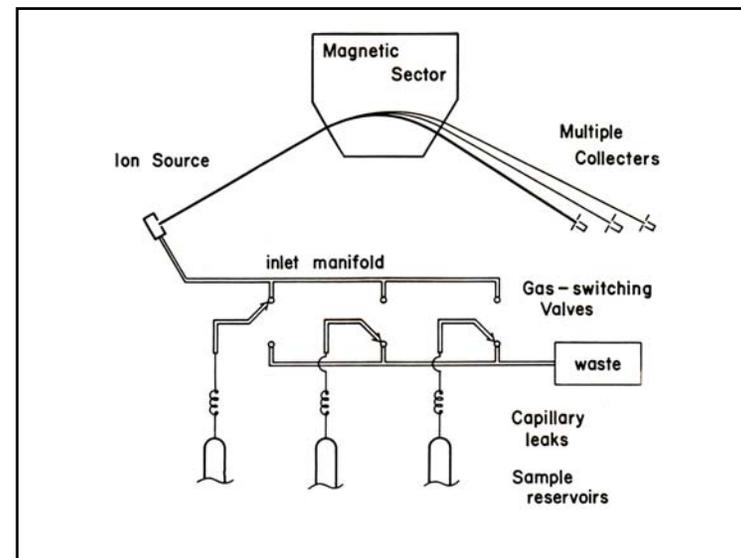
\*or a smooth, reproducible, quantifiable function determined by varying size standards

## Peak Height Manometry and Isotope Dilution

- Since MS is basically ratiometric:
  - It measures ratios better than peak heights
  - Use ISOTOPE DILUTION:
    - Add an aliquot of isotopically “different” spike to sample
    - Compare mixture to comparable standard
    - Solve multiple equations (in isotope ratios) for size
    - Need at least 2 isotopes, preferably more
    - Depends on isotope ratio difference of spike
      - Propagation of errors!

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Molecular-Ion Multiplets  
Carbon Dioxide as an Example

Mass 44:  $^{12}\text{C}^{16}\text{O}_2$

Mass 45:  $^{13}\text{C}^{16}\text{O}_2$ ,  $^{12}\text{C}^{17}\text{O}^{16}\text{O}$

Mass 46:  $^{13}\text{C}^{17}\text{O}^{16}\text{O}$ ,  $^{12}\text{C}^{18}\text{O}^{16}\text{O}$ ,  $^{12}\text{C}^{17}\text{O}_2$

Mass 47:  $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ ,  $^{13}\text{C}^{17}\text{O}_2$ ,  $^{12}\text{C}^{18}\text{O}^{17}\text{O}$

Mass 48:  $^{13}\text{C}^{18}\text{O}^{17}\text{O}$ ,  $^{12}\text{C}^{18}\text{O}_2$

Mass 49:  $^{13}\text{C}^{18}\text{O}_2$

Isotopes distributed randomly. See "Isotopic Contributions to Ion Currents in Molecular-Ion Multiplets." The task is to convert observed, ion-current ratios to isotope ratios.

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## Measuring Half-Lives

With  $t_{1/2} > 1 \text{ Ka}$ , hanging around is no option.

So how to do it?

1. Take a precisely known amount of a standard and measure its activity
  - a. For example OXI (a radiocarbon standard measured by NIST by calibrated radiation counters)
  - b.  $A = \lambda N$ , but to get  $N$  you need to know absolute  $R=^{14}\text{C}/^{12}\text{C}$
2. Create an artificial standard with known isotope ratio
  - a. First by counting the number of  $^{14}\text{C}$  atoms implanted using AMS (e.g., with a beam of known luminosity of  $^{14}\text{C}$  ions/sec into a copper foil target)
  - b. Mix the sample (by dissolving the Cu foil) with a known amount of  $^{14}\text{C}$ -free  $^{12}\text{C}$  &  $^{13}\text{C}$  (using very old  $\text{CO}_2$ )
3. Using AMS compare the two standards. You get absolute ratio of NIST standard and can calculate  $\lambda$  from step 1.

Recent half-life checks by this method:  $^{14}\text{C}$ ,  $^{10}\text{Be}$ ,  $^{60}\text{Fe}$

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