Mass Spectrometry Detectors, A/D, Signal-to-Noise

CHEM-5181
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Why is Mass Spectrometry so Successful? Aka, what must we have or we are doomed?

Because of its:

A. High Sensitivity
   – ability to detect very small amounts

B. High Selectivity
   – Ability to tell molecules apart in a mixture

C. High Time Resolution

D. Low Cost

E. I don't know
Direct Current Detection: “Faraday Cup”

Clicker Q

- With a quadrupole, we want to measure an ion current at an $m/z$ of interest, which we know is of the order of 100 Hz (100 ions/sec).
- We use the best available current meter, which has a noise level of 0.4 fA in 1 second
- How long will we need to integrate to obtain a signal-to-noise ratio of 10?
  - Hint: the signal to noise increases as the square root of the averaging time for counting processes (Poisson statistics)
  A. 1 second
  B. 1 minute
  C. 1 hour
  D. 1 day
  E. 1 millennium
The Challenge of Ion Detection

- Faraday Cup works for large ion currents (slow)
- 1 ion: $1.6 \times 10^{-19}$ C
- 1 ion / second: $1.6 \times 10^{-19}$ A = $1.6 \times 10^{-4}$ fA
- Most sensitive direct current measurements:
  - Keithley Model 6430 “The measurement industry’s lowest noise”: 0.4 fA
  - Detection limit is 7,500 ions/s!
- Key: detectors that can amplify ion signals directly above this range
  - E.g. if amplify by $10^6$ w/o noise, have SNR ~ 400

Desirable Detector Properties

- High amplification
- Fast time response
- Low noise
- High collection efficiency
- Low cost
- Narrow distribution of responses
- Same response for all masses
- Large dynamic range
- Long term stability
- Long life
- Mounted outside of the vacuum if possible
Electron Multiplier Notes

- An ion strikes the first dynode, resulting in the emission of several electrons. These secondary electrons are then attracted to the second dynode, where each electron produces several more electrons, and so on.
- Most commonly used detector
- Very high sensitivity
- Very low noise
- Typical gain of $10^6$, life of 1-2 years
Clicker Q

- With a quadrupole, we want to measure an ion current at an m/z of interest, which we know is of the order of 0.1 Hz (0.1 ions/sec).
- We have decided to splurge and invest in an electron multiplier, which has a gain of $10^6$, and then connect its signal to the current meter with noise level of 0.4 fA.
- How long will we need to integrate to obtain a signal-to-noise ratio of 10?
  - Hint: the signal to noise increases as the square root of the averaging time for counting processes (Poisson statistics)
  A. 1 μs
  B. 1 ms
  C. 25 ms
  D. 1 second
  E. 1 hour

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**Continuous Dynode Electron Multiplier**

From Watson

**FIG. 13.3.** Conceptual diagram of a nonmagnetic electron multiplier; the field gradient along the resistive conductive internal surface of the cornucopia attracts the cascading electrons toward the preamplifier.
Array Detector

- Especially useful for high m/z ions, as EM response decays quickly

**Figure 2.22** Illustration of the operation of an array detector.

Conversion Dynode

- Especially useful for high m/z ions, as EM response decays quickly

**Figure 2.21** High-energy dynode detector.
High $m/z$ Detectors

- Issue for e.g. proteomics
  - Traditional detectors lose response at very high $m/z$
- Active research field right now


Postacceleration (Daly Knob) Detector

From Watson

FIG. 13.4. The Daly detector is a manifestation of a postacceleration detector that provides the advantage of external access to all components of the detector except the Daly knob. The secondary electrons from the Daly knob impact a phosphor, which emits photons that enter a photomultiplier.
Photomultiplier Detector Notes

- Amplification $10^4$-$10^5$
- Advantages:
  - Longer lifetime
  - Replaceable components are external to the vacuum

Microchannel Plate Detector

Figure 2.60
Cross-section of an array plate and electron multiplication within a channel. (Reproduced from Galileo documentation, with permission)
A typical MCP consists of ~10,000,000 closely packed channels of ~10 microns diameter and has thickness of ~1 mm.
Channels are parallel and often enter the plate at a small angle to the surface (~8° from normal).
Due to the angle, an ion that enters one of the channels is guaranteed to hit the wall of the channel. The impact frees several electrons, which are accelerated along the channel until they in turn strike the channel surface, giving rise to more electrons.
Eventually this cascade process yields a cloud of several thousand electrons which emerge from the rear of the plate.
The large planar detection area of MCPs results in a large acceptance volume. And, only a few MCP channels out of millions are affected by the detection of a single ion, thus it is possible to detect many ions at the same time.

MCP Notes 2

- The governing physical parameter which determines gain is the L/D ratio (length to diameter of the individual channels). The higher the ratio, the higher the gain. Typical values are in the range 75:1 - 175:1.
- Gain is also a function of the electron accelerating potential, $V_F - V_B$.
- To increase gain, most MCP detectors use two plates with angled channels rotated 180° from each other producing a chevron (v-like) shape. In this configuration, gains reach $10^6$ to $10^7$.
- Electrons exiting the rear of the back plate collide with a metal anode, leading to a measurable current in the signal line.
- The current is recorded directly, or more typically as a proportional voltage (e.g., ToF-AMS).
### Part 2: Analog-to-Digital Conversion and Signal-to-Noise

#### Comparison of Detectors

<table>
<thead>
<tr>
<th>Detector</th>
<th>Advantages</th>
<th>Disadvantages</th>
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</thead>
<tbody>
<tr>
<td>Faraday cup</td>
<td>Good for checking ion transmission and detector sensitivity</td>
<td>Low amplification (~10)</td>
</tr>
<tr>
<td>Scintillation counter</td>
<td>Extremely robust</td>
<td>Cannot be exposed to light</td>
</tr>
<tr>
<td></td>
<td>Long lifetime (&gt;5 years)</td>
<td></td>
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<tr>
<td></td>
<td>Good sensitivity (~106)</td>
<td></td>
</tr>
<tr>
<td>Electron multiplier</td>
<td>Fast response</td>
<td>Short lifetime (1–2 years)</td>
</tr>
<tr>
<td></td>
<td>Sensitive (~106)</td>
<td></td>
</tr>
<tr>
<td>High-energy dynodes with electron multiplier</td>
<td>Increases high mass sensitivity</td>
<td>May shorten lifetime of electron multiplier</td>
</tr>
<tr>
<td>Array</td>
<td>Fast and sensitive</td>
<td>Low resolution ~0.2 Da</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expensive</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Short lifetime (~1 year)</td>
</tr>
<tr>
<td>FT-MS</td>
<td>Mass analyzer is the detector</td>
<td>Used only with FT-MS instruments</td>
</tr>
<tr>
<td></td>
<td>High resolution (~500,000)</td>
<td></td>
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</table>
**Time-to-Digital Converter (TDC)**

A TDC converts a signal of sporadic pulses into a digital representation of their time indices. Neither the height nor the area of the pulse is recorded. Thus, TDCs are used when the important information is to be found in the timing of events. A TDC usually follows a discriminator, which sets the minimum accepted pulse amplitude. TDCs are most often used in applications where measurement events happen infrequently, because individual events cannot be distinguished from simultaneous events. ToF-MS experiments with low ion currents can use TDC to “count” ion arrival events. Peaks heights in MS develop through averaging. Has advantage that recorded peak has width independent of MCP pulse width – i.e., higher mass resolution at low m/z.


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**Analog-to-Digital Converter (ADC)**

An analog-to-digital converter is an electronic circuit that converts continuous signals to discrete digital numbers.

*Records time and amplitude of waveform events.*

The analog signal is continuous in time and it is necessary to convert this to a flow of digital values. It is therefore required to define the **sampling rate** at which new digital values are sampled from the analog signal.

The **resolution** of the converter indicates the number of discrete values it can produce over the range of voltage values.

Resolution is usually expressed in bits. For example, the ToF-AMS ADC encodes an analog input to one of 256 discrete values (0..255), which is 8-bit resolution.

Demo from [Learning by Simulation](http://www.vias.org/simulations/simusoft_adconversion.html). By Hans Lohninger
Clicker Q

- \( m/z \) 100 is detected as a 5 ns wide peak in a TOFMS, where individual ions have pulse widths of 1 ns. The repetition rate of the spectrometer is 50 kHz, and the ion rate at that \( m/z \) is 10 kHz. Can we use a TDC to record this signal?
  A. Yes, with no loss of linearity
  B. Yes, with a little loss of linearity
  C. Yes, but with large loss of linearity
  D. No
  E. I don’t know

Signal and Noise

- **Signal-to-Noise Ratio**
  - \( \text{SNR} = \frac{\text{signal amplitude}}{\sigma_{\text{noise}}} \)
  - \( \text{SNR} = 3 \), detection limit (DL)
  - \( \text{SNR} = 10 \), limit of quantification

![SNR graph]
Sources of Environmental Noise

Afternoon  Night  Morning

Noise in thermogravimetric analysis as a function of time

Some typical noise sources:


Signal-to-Noise Enhancement

• Signal Averaging
  – http://www.vias.org/simulations/simusoft_spectaccu.html
Filtering

In hardware:

Digitally (typically in software):

Electrical Noise Pickup & Shielding

- E.g. capacitance coupling
  - Current flowing in one wire (e.g. power) induces an image charge in signal cable
  - Shielding is critical, especially at high frequencies or with weak signals

Figure 6.126 (a) Capacitive coupling between two wires; (b) the equivalent electrical circuit with the effect of wire 1 on wire 2 represented by C.

Figure 6.127 Shielding to prevent capacitive coupling.

From Moore, Building Scientific Apparatus, 3rd Ed
Power Line-Coupled Noise

- Lots of things are connected to power systems

![Diagram of three circuits on a common power line.](image)

- Large current changes of some components induce noise in others
- “60 Hz noise”, “Friday afternoon noise”
- Aircraft power has been cleanest I’ve seen!

Grounding & Ground Loops

- Grounding issues are among the most pervasive and confusing experimental issues
  - If you do experiments, you will run into this
  - Invest the time to learn about it ahead of time!

- Moore, Building Sci. Apparatus; Ott: Electromagnetic Compatibility Engineering