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

CHEM-5181

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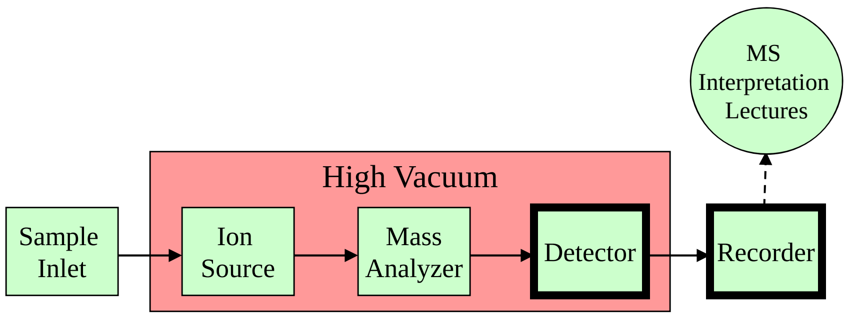


Why is Mass Spectrometry so Succesful? Aka, what must we have or we are doomed?

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"

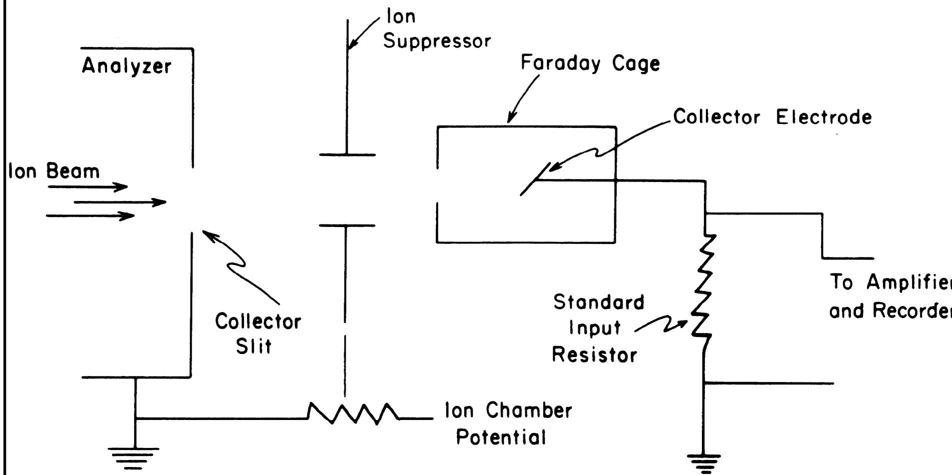


FIG. 13.1. Conceptual diagram of Faraday-cup detector. (From Watson JT. Mass spectrometry instrumentation. In: Waller GR, ed. *Biochemical Applications of Mass Spectrometry*. Wiley-Interscience, New York, 1972, with permission.)

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

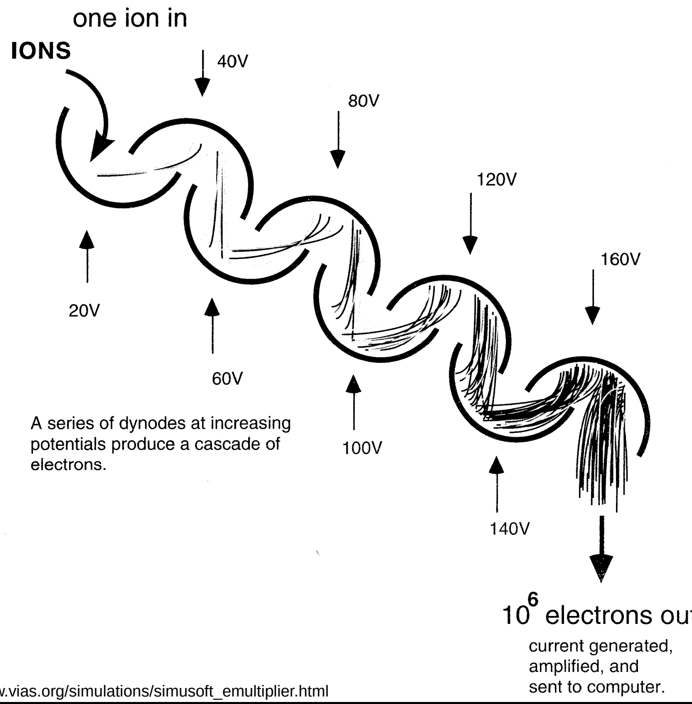
The Challenge of Ion Detection

- Faraday Cup works for large ion currents (slow)
- 1 ion: 1.6×10^{-19} C
- 1 ion / second: 1.6×10^{-19} A= 1.6×10^{-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

Principle of the (Discrete) Electron Multiplier



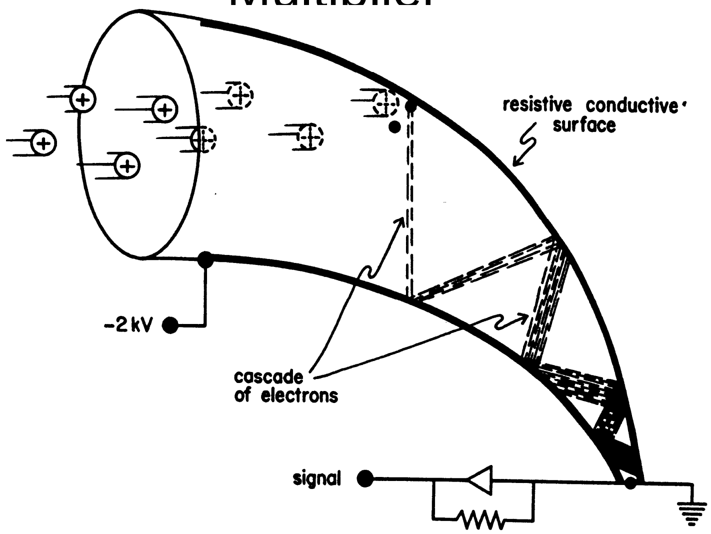
From Siudzak

http://www.vias.org/simulations/simusoft_emultiplier.html

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

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.

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

Array Detector

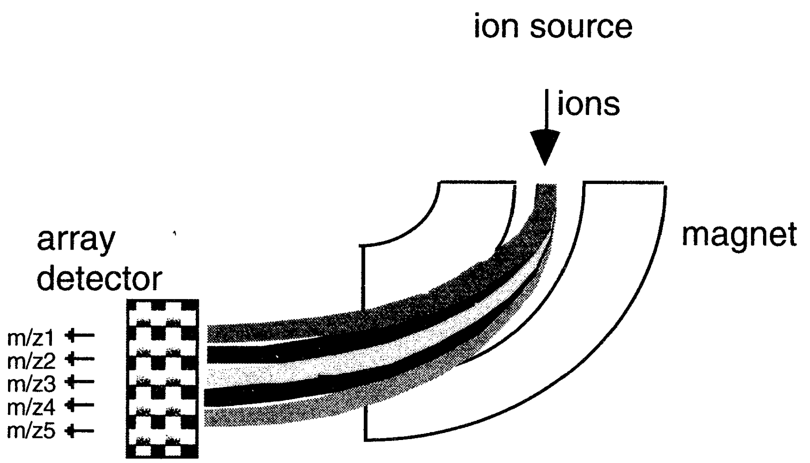


Figure 2.22 Illustration of the operation of an array detector.

From Siudzak

Conversion Dynode

From Siudzak

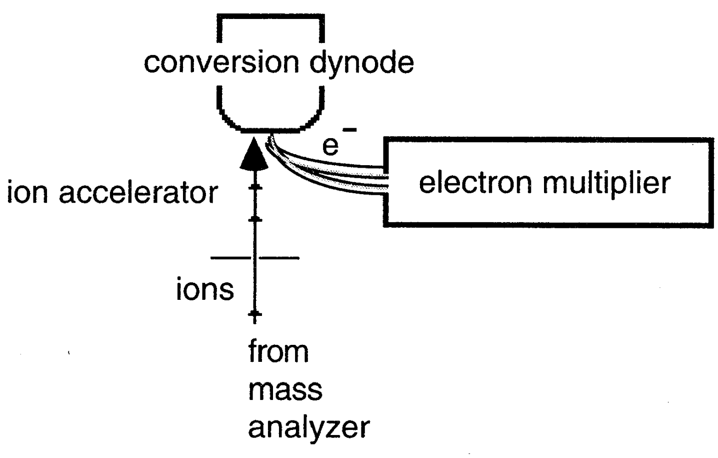
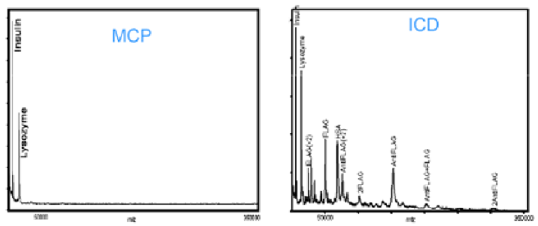


Figure 2.21 High-energy dynode detector.

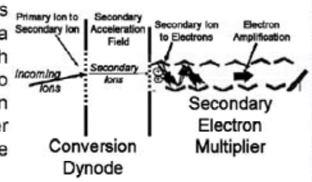
- Especially useful for high *m/z* ions, as EM response decays quickly

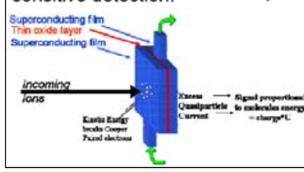
High *m/z* Detectors

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



ICD generates secondary ions at a dynode surface which are reaccelerated into a secondary electron multiplier as higher velocity ions for more sensitive detection.

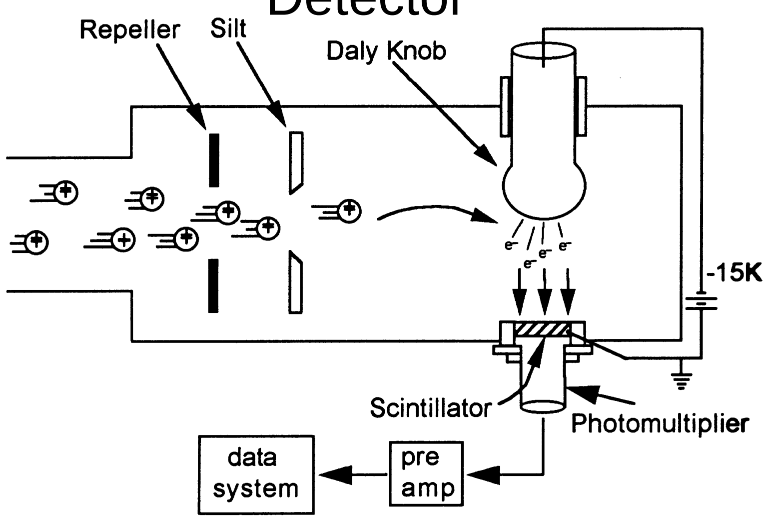




STJ works by measuring the kinetic energy of the incoming ions which in TOF-MS is mass independent.

Comparison of Sensitivity and Saturation of MALDI-TOF Detectors for High Mass Ions. Ryan J. Wenzel, Susanne Kern and Renato Zenobi. ASMS 2006 and 2007. http://www.covalx.com/covalx/files/scientificreports/ASMS06-Wenzel.pdf

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

From Hoffmann

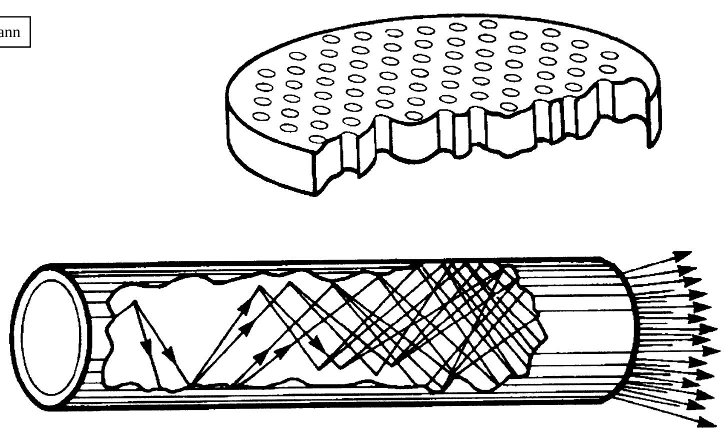
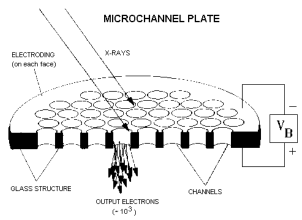
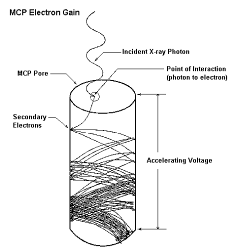
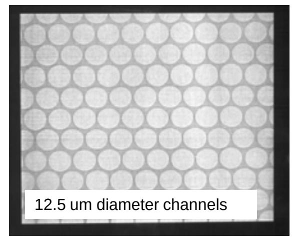


Figure 2.60
Cross-section of an array plate and electron multiplication within a channel. (Reproduced from Galileo documentation, with permission)

MCP Notes






12.5 um diameter channels

(Images from: http://hea-www.harvard.edu/HRC/mcp/mcp.html)

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).

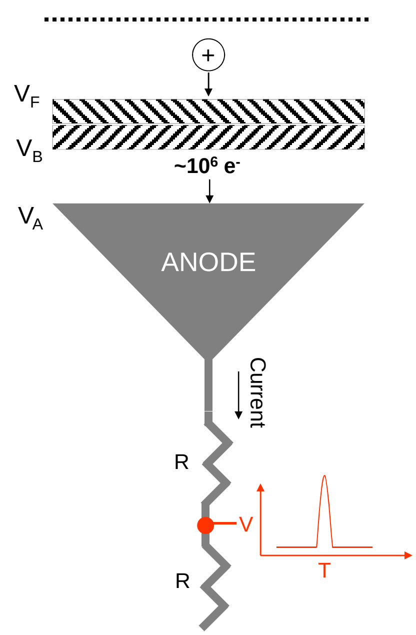
Due to the angle, an ion that enters one of the channels is guaranteed to hit the wall of the channel. The impact frees several electrons, which are accelerated along the channel until they in turn strike the channel surface, giving rise to more electrons.

Eventually this cascade process yields a cloud of several thousand electrons which emerge from the rear of 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 times.

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).



Comparison of Detectors

TABLE 2.3
General Comparison of Ion Detectors

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

From Siudzak

Part 2: Analog-to-Digital Conversion and Signal-to-Noise

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.

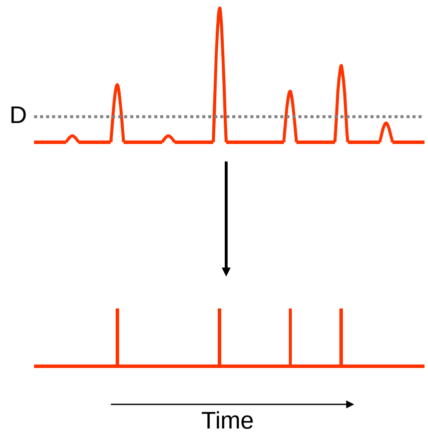
Thus, TDCs are used when the important information is to be found in the timing of events.

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.



See http://en.wikipedia.org/wiki/Time_to_digital_converter

Analog-to-Digital Converter (ADC)

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

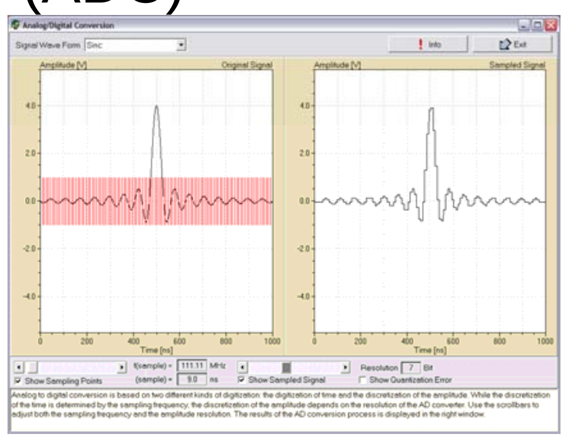
Records time and amplitude of waveform events.

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.



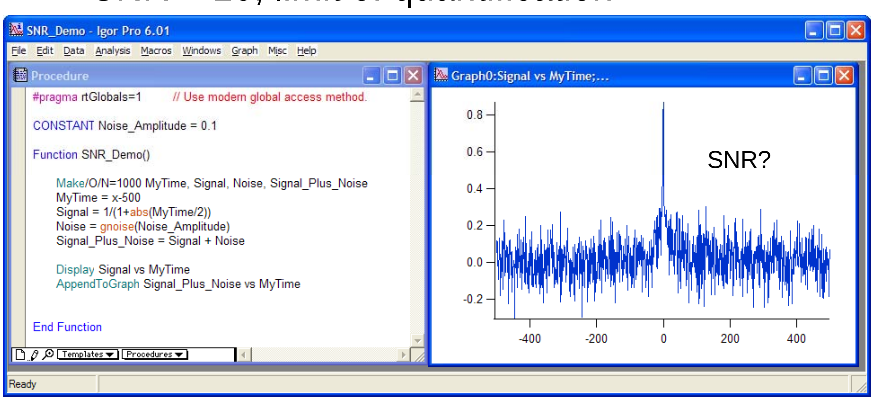
Demo from *Learning by Simulation.* By Hans Lohninger (http://www.vias.org/simulations/simusoft_adconversion.html)

Clicker Q

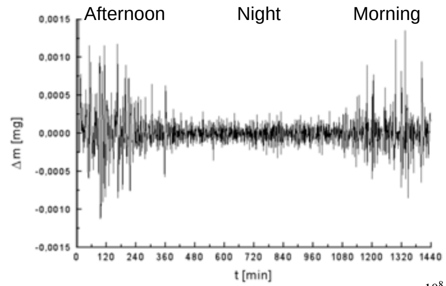
- *m/z* 100 is detected as a 5 ns wide peak in a TOFMS, where individual ions have pulse widths of 1 ns. The repetition rate of the spectrometer is 50 kHz, and the ion rate at that m/z is 10 kHz. Can we use a TDC to record this signal?
  A. Yes, with no loss of linearity
  B. Yes, with a little loss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

Signal and Noise

- Signal-to-Noise Ratio
  - SNR = signal amplitude / σ_{noise}
  - SNR = 3, detection limit (DL)
  - SNR = 10, limit of quantification



Sources of Environmental Noise



Noise in thermogravimetric analysis as a function of time

http://en.wikipedia.org/wiki/Signal-to-noise_ratio

Some typical noise sources:

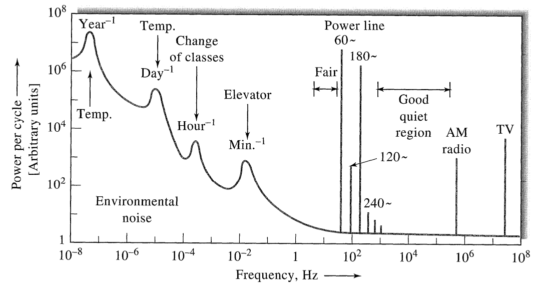
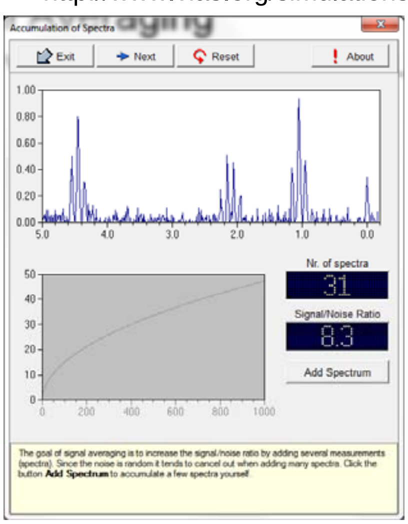
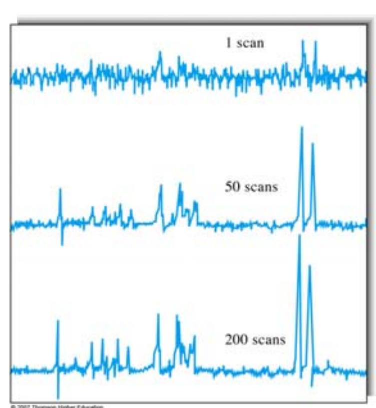


FIGURE 5-3 Some sources of environmental noise in a university laboratory. Note the frequency dependence and regions where various types of interference occur. (From T. Coor, *J. Chem. Educ.*, **1968**, *45*, A540. With permission.)

Signal-to-Noise Enhancement

- Signal Averaging
  - http://www.vias.org/simulations/simusoft_spectaccu.html

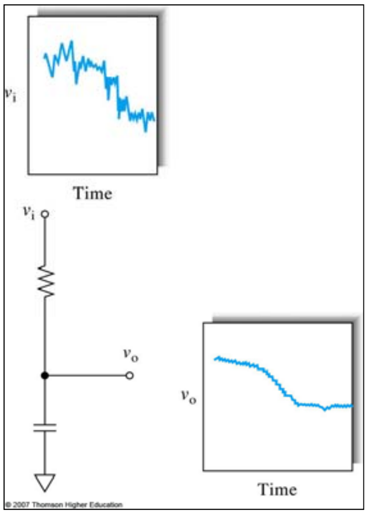




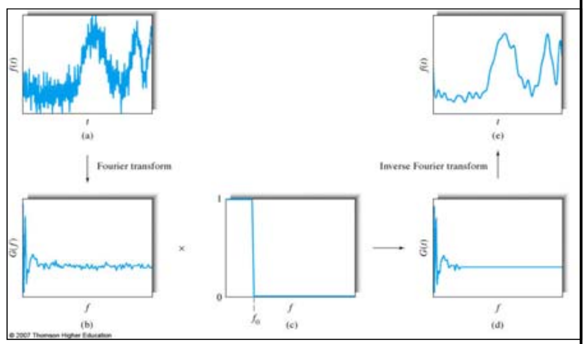
From Skoog, Fig. 5-10

Filtering

In hardware:



Digitally (typically in software):



From Skoog, Fig. 5-5 and 5-12

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

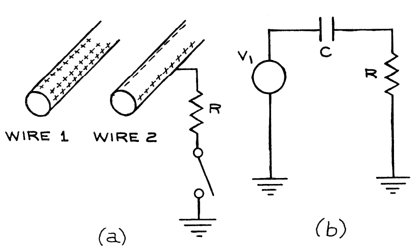


Figure 6.126 (a) Capacitive coupling between two wires; (b) the equivalent electrical circuit with the effect of wire 1 on wire 2 represented by C.

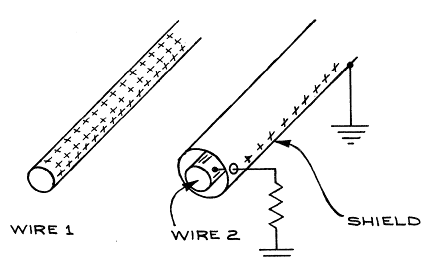


Figure 6.127 Shielding to prevent capacitive coupling.

From Moore, Building Scientific Apparatus, 3rd Ed

Power Line-Coupled Noise

- Lots of things are connected to power systems

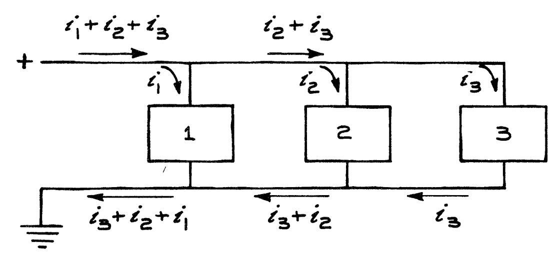


Figure 6.128 Three circuits on a common power line.

- 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

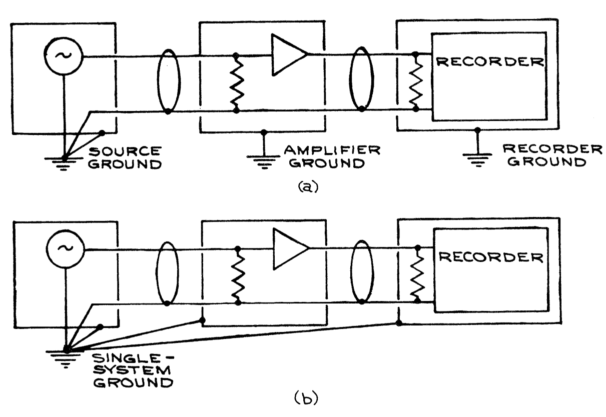


Figure 6.129 System grounding: (a) multiple grounds; (b) single ground to eliminate ground loops.

- Grounding issues are among the most pervasive and confusing experimental issues
  - If you do experiments, you will run into this
  - Invest the time lo learn about it ahead of time!
    - Moore, Building Sci. Apparatus; Ott: Electromagnetic Compatibility Engineering