CHEM 524 -- Course Outline (Part 10) – Signal to Noise —2013

For html of 2005 notes with linked figures, click here

VII. Signal to noise considerations (*Text - Chap. 5*)

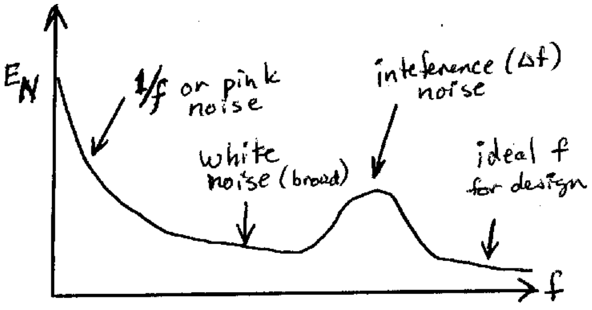
A. Noise definitions:

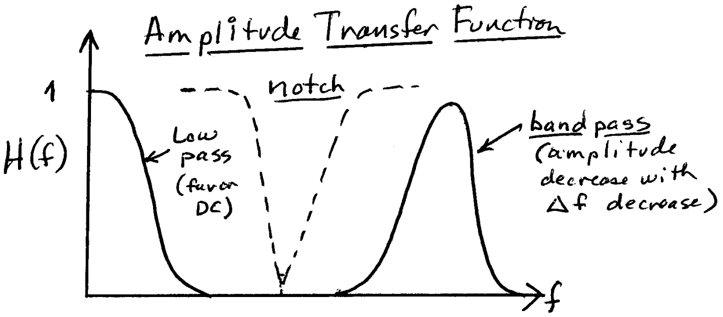
- Average signal of several measurements: $\tilde{\tilde{E}} = \Sigma E_i/n$
- Standard deviation (rms excursion from mean): $E_{rms} = \sigma_E = [\Sigma (E_i - \tilde{E})^2/(n-1)]^{1/2}$
- random -- non-correlated to other aspects of measurement
- fundamental -- intrinsic to detection method or to photon flux
- chemical -- errors in sampling

1. Types

- white (Gaussian), ubiquitous to light fluctuation, random at all detection frequencies can be intrinsic to light (shot noise $\sim n^{1/2}$) or detector (constant or dark noise)
- pink (1/f), -- diode detectors (e.g. MCT) show this, often become constant at ~1kHz
- interference (at f) –could be many things, e.g. line frequency, radio stations, neighbors
- flicker (~signal) – typically chemical or due to instrument stability issues

a. evaluate by understanding noise power spectrum –particular to experiment/instrument





b. use to design modulation or detection scheme – choose optimal frequency to operate

c. Amplitude transfer function (book: Table 5-1, Fig. 5-4)

- mathematical representation of device efficiency as function of frequency: $H(f) = E_{out}/E_{in}$
- band pass: $\Delta f = \int |H(f)|^2 df$ -- frequency range with attenuation < 3dB or $H(f) < 0.707$
- effect on noise: $\sigma_E^2 = \int P(e)|H(f)|^2 df$ where P(e) -- density spectrum
    - -- white noise: $\sigma_E^2 = P(e)\Delta f$ - since P(e) const
- time constant -- low pass at f = 0 -- DC/stability trade off
    - wait 5τ to make measurement, *rule of thumb*: $\tau < 1/10$ measurement time
    - integrating circuit effectively faster, can improve S/N in same time and can reject interfering signals

B. Quantum/shot noise -- square root dependence on signal level (also Schottky noise)
due to random photon field and random probability of emission of e^- at interface

- PMT: signal depends on number of photons or photo electrons, n_p

  Signal: $\phi = n_p$, Noise: $\sigma_p = n_p^{1/2}$, → S/N = $\phi/\sigma_p = n_p^{1/2}$, ("pure" noise, intrinsic)

- cathode: $(S/N)_n = n_C/\sigma_C = K\, n_p/(K\, n_P)^{1/2} = (Kn_p)^{1/2}$, in current: $i_C/\sigma_C = (i_C t/e)^{1/2}$ (K~q.eff)

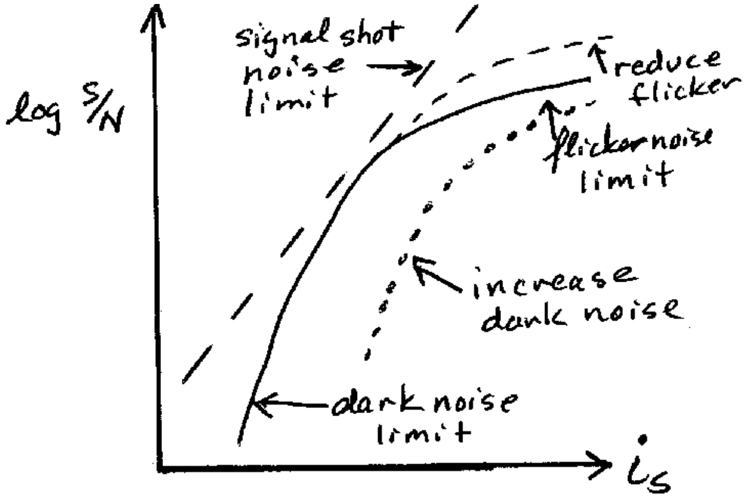
- anode: $\sigma_E = [2e\Delta f(1+\alpha)mGE]^{1/2}$, m - multiplier, G - gain in V/A, E - signal ($R\cdot\phi$),

  α → multiplier adds to noise [vary 0.1-0.5, good PMT ~ $(\delta-1)^{-1}$, δ - gain per dynode]

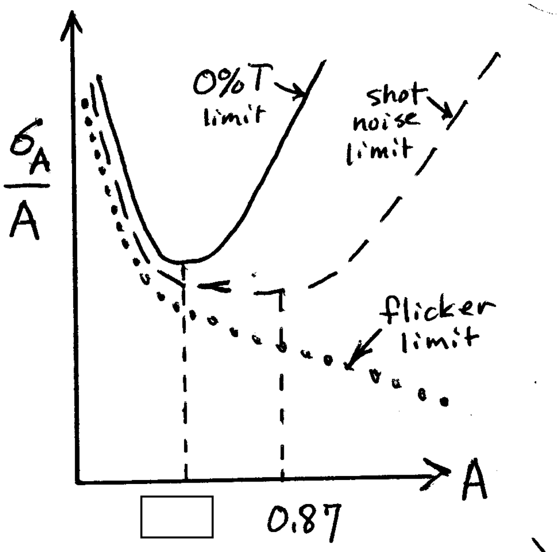
C. Other noise sources

1. Flicker, due to sample or blank variation - *non-fundamental*, plus especially source or temperature fluctuations → impact the signal level, noise level ~ light signal: $\sigma_F \sim E_S$
2. Dark current (e.g. field emission dynode or amplifier output level) -- excess noise, additive – independent of light level – note: not necessarily "white" can have spectrum
3. Quantization noise (finite digital resolution) – for q = quantization level, if $\sigma > q/2$ →
   $\sigma_q = q/12^{1/2}$ (if σ from other sources is less, then limit by readout resolution, $\sigma_q = q/2$)
4. Thermal (Johnson) noise - (thermal fluctuation of e^- in resistor) $\boldsymbol{\sigma_J = (4kTR\Delta f)^{1/2}}$ →
   a. Effectively "white" (constant with f) at practical detection frequencies
   b. *cooling, narrowing band pass* help, smaller $\boldsymbol{\sigma_J}$ so less noise higher S/N
   c. lowering R also, but usually costs signal (in volts)
5. Uncorrelated sources, sum the noise terms: $N \sim [\sigma_e^2 + \sigma_F^2 + \sigma_q^2 + \sigma_J^2 + \ldots]^{1/2}$
   a. (read Section 5.4, 5.5)

D. ***Bottom line*** -- understand Figures relating S/N and E (fig. 5.6), A/σ_A vs A (fig. 5.7)



S/N Variations (Emission)



S/N variation (Absorption)

1. Emission—different noise sources approach the ideal shot-noise limit

    a. Shot noise limit: $S/N = i_S/[K(i_S+i_d)]^{1/2}$ → $K=2e\Delta f(1+\alpha)$ K-unit corr., α-PMT mult. noise
    —to improve → reduce Δf and/or dark current, i_d

    b. Dark noise (or Signal) limit: $S/N = i_S/(Ki_B)^{1/2}$ - Add $(Xi_B)^2$ if flicker, *to improve inc. S*
    (or decrease dark noise by cooling detector or improving readout/amp or similar)

    c. Flicker limit: $S/N = \zeta^{-1}$ — becomes *constant S/N* at high S

2. Absorption—ratioing I and I_0 makes more complex: $\sigma_A = 0.43\sigma_T/T$ from $A = -0.43 \ln T$

    a. $(S/N)^{-1} = \sigma_A/A = -\sigma_T/T\ln T$ --new form for plots (inverse), *lower is better* in this view

    b. 0%T limiting conditions—dark or amp. or readout limited — min 0.43 A (Fig wrong!)
    reduce dark noise, IR this dominates—cool detector

    c. Shot noise limited—min 0.87 A –reduce bandwidth, increase light level

    d. Flicker—since constant, improves with absorbance, but not real,
    since losing light → will become dark noise limited

E. Enhance S/N

1. Filtering ---time domain

    a. average e.g. multiplex -- time avg. idea, integrate signals in each channel
    - multiple (n) scan average, increase $S/N = n^{1/2}$

    b. time constant—attenuate the high frequency components to enhance the DC

2. Filter -- frequency domain (use Δf - select signal, attenuate noise →bandpass or lock-in)

    a. best: digitize time varying signal, FT to frequency space (i.e. $t \rightarrow \nu$ transform)

    b. multiply by H(f), and back transform to signal representation, E(t)

3. Adjust levels – i.e. change (increase) signal level or reduce noise level

    a. Shot-noise limit (raise to flicker limit),

    b. Dark limit (cool detector, get better amps, readout),

    c. flicker (adjust instrument, e.g. double beam -- counter drift, long time changes – measure signal and blank simultaneously)

4. Photon counting -- best for low light level -- $(S/N)_{PC}/(S/N)_i = [f_d(1+\alpha)]^{1/2}$,

    a. f_d discriminator coeff., fraction anodic pulses passed,

    b. $(1+\alpha)$ term gives 5-25% improvement

5. Modulation -- demodulate with lock-in, boxcar, or correlation –

    a. Modulation can be major advantage when dark noise and 1/f noise limited—these are additive noise, not modulated, independent of signal, so eliminated

    b. all discriminate against noise which is broad band and no time correlation to signal (except flicker) - (Fig. 5-9)

Homework

Discussion questions: Chap 5 - #5, 6, 7, 8, 9, 11, 13, 14, 15, 16, 19

To hand in: Chap 5 - #2, 4, 10, 17