I1 Spect Introd 971129 mon

Signal to noise ratio:

$$\frac{S}{N} = \frac{i_s}{\{k(i_s + i_B + i_d) + (\xi i_s)^2 + (\chi i_B)^2 + [(\sigma_d)_{ex}/mG]^2 + (\sigma_{ar}/mG)^2\}^{1/2}}$$

Shot n. — Analyte flick n. — Backgr fl. n. — dark flick n. — amplif. readout.

- Luminesc. and/or Emission

* Blank noise limited ([Analyte]↓↓)

(1) Shot noise (high quality instr.)
(2) nonfund. n. l.
(3) Backgr. S. n. li.
(4) Detector noise limited.

* Analyte Signal noise limited — i_s ← (Analyte)↑

$$T = \frac{E_{st} - E_{ot}}{E_{rt} - E_{ot}} = \frac{E_s}{E_r}$$

$E_s = T E_r$

σ_A:
- $\propto 1/\sqrt{T}$ — Shot
- $\propto$ const. — flick.
- $\propto \frac{1}{T}$ — 0%T ✓

σ_T:
- $\propto \sqrt{T}$ — Shot
- $\propto T$ — flick
- $\propto$ const. — 0%T

$T_1 = 0.8$ $\quad \frac{1}{T_1} = 1.25$ $\quad$ 0.04

$T_2 = 0.4$ $\quad \frac{1}{T_2} = 2.5$ $\quad$ ↓ 0.08

Analytical signal limited S/N expression (Fluor or Emiss, high concn)

$$\frac{S}{N} = \frac{i_S}{\{K(i_S + \cancel{i_B} + \cancel{i_d}) + (\xi i_S)^2 + (\chi \cancel{i_B})^2 + [(\cancel{\sigma_a)_{ex}/mG}]^2 + (\cancel{\sigma_a/mG})^2\}^{1/2}}$$

$$\frac{S}{N} = \frac{i_S}{\{K(i_S) + (\xi i_S)^2\}^{1/2}}$$

1- **Analytical signal shot noise limited** S/N expression:

$$\frac{S}{N} = \left(\frac{i_S}{K}\right)^{1/2}$$

2- **Analytical signal flicker noise limited** S/N expression: here S/N can be improved by reducing bandwidth or adjusting experimental condition. Increasing signal does not improve S/N in such condition:

$$\frac{S}{N} = \xi^{-1}$$

from p149

Dependence of S/N on analytical signal:

$$\frac{S}{N} = \frac{i_S}{\{K(i_S + i_B + i_d) + (\xi i_S)^2 + (\chi i_B)^2 + [(\sigma_d)_{ex}/mG]^2 + (\sigma_{ar}/mG)^2\}^{1/2}}$$

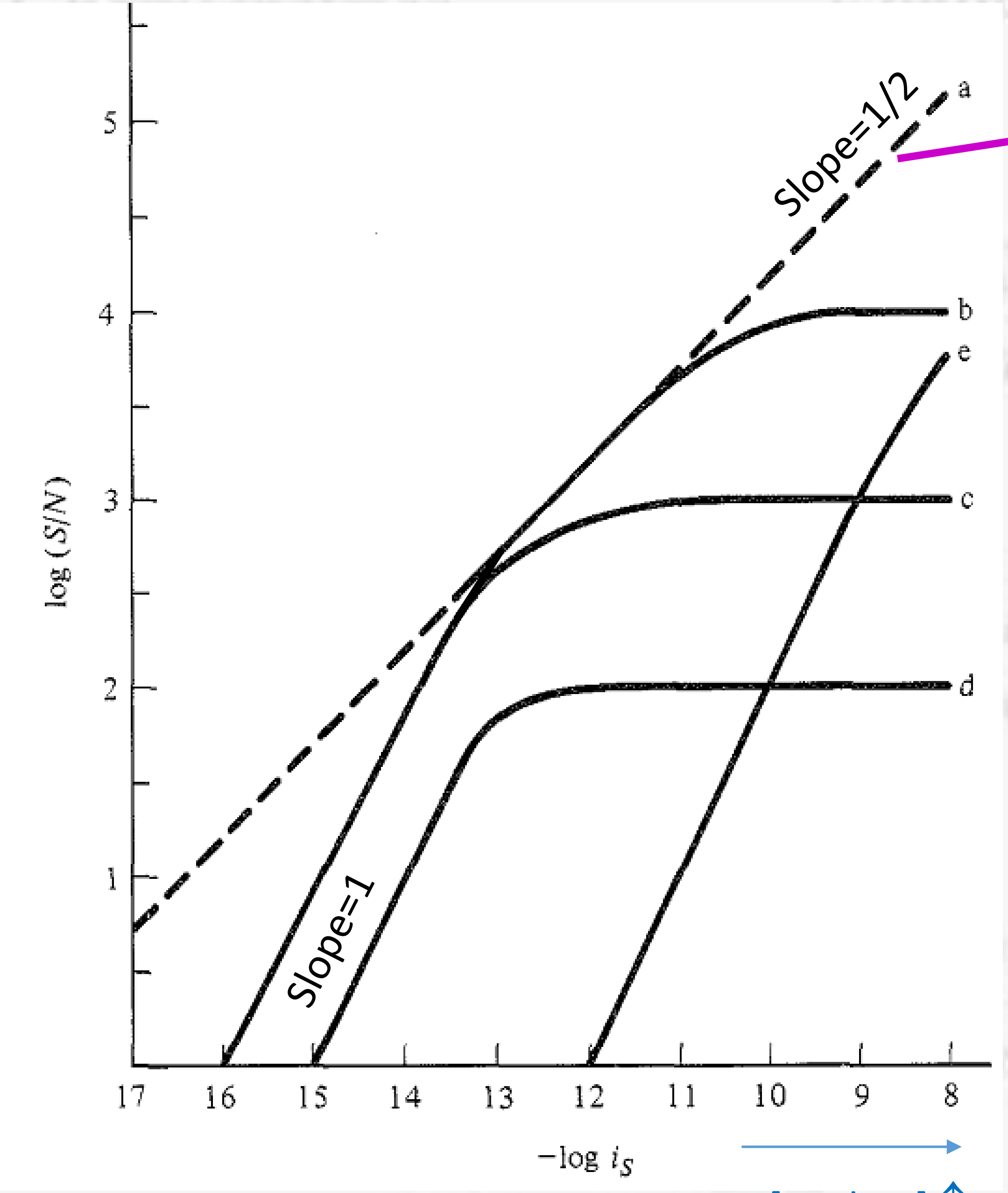
Blank includes parts that are **independents** of i_s

$$\frac{S}{N} = \frac{i_S}{[Ki_S + (\xi i_S)^2 + \sigma_{bk}^2]^{1/2}}$$

1- Shot noise limited: $\frac{S}{N} = \frac{i_S^{1/2}}{[K]^{1/2}}$ → $\log\frac{S}{N} = \log[K]^{1/2} + 1/2 \log i_s$

2- Flicker noise limited: $\frac{S}{N} = \xi^{-1/2}$ → $\log\frac{S}{N} = -1/2 \log \xi + 0 \log i_s$

3- Blank noise limited: $\frac{S}{N} = \frac{i_S}{\sigma_{bk}}$ → $\log\frac{S}{N} = -\log \sigma_{bk} + \log i_S$



[analyte] ↑

Limit line for S/N is the shot noise.

$\xi=10^{-2}$, $\sigma_{bk}=10^{-16}$

$\xi=10^{-2}$, $\sigma_{bk}=10^{-12}$

$\xi=10^{-3}$, $\sigma_{bk}=10^{-16}$

$\xi=10^{-2}$, $\sigma_{bk}=10^{-15}$

When σ_{bk} and/or ξ are/is high we do not observe shot noise.
(low quality instrument)

Signal to noise expression for absorption (vs T):

A=-log T or A=-0.43 ln T → $\sigma_A = 0.43\frac{\sigma_T}{T}$

$$T = \frac{E_{st} - E_{0t}}{E_{rt} - E_{0t}}$$

by considering only σ_{st}

$$\frac{d(\frac{U}{V})}{dx} = \frac{U'V - UV'}{V^2}$$

$$\sigma_T = \frac{\sigma_{st}(E_{rt} - E_{0t}) - (E_{st} - E_{0t})(0)}{(E_{rt} - E_{0t})^2} = \frac{\sigma_{st}}{E_r}$$

$$\sigma_A = 0.43\frac{\sigma_{st}}{TE_r}$$

$$E_{st} = E_s + E_{0t}$$

$$\sigma_T = \frac{\sigma_{st}}{E_r} = \frac{(mGE_s + (\xi E_s\ )^2 + \sigma_{0t}^2)^{1/2}}{E_r}$$

$$\sigma_T = \frac{\sigma_{st}}{E_r} = \frac{(mGTE_r + (\xi TE_r\ )^2 + \sigma_{0t}^2)^{1/2}}{E_r}$$

- $\sigma_T \propto \sqrt{T}$ → **Shot noise limitin**
- $\sigma_T \propto T$ → **Fliker noise**
- $\sigma_T \propto$ constant → **Dark noise limited**

Signal to noise expression for absorption (vs A):

Noise equation for Transmitance is exactly similar to luminesc & emission.

$$\sigma_T = \frac{\sigma_{st}}{E_r} = \frac{(mGTE_r + (\xi TE_r)^2 + \sigma_{0t}^2)^{1/2}}{E_r}$$

in

$$\sigma_A = 0.43\frac{\sigma_T}{T}$$

But for absorbance it is different:

$$\sigma_A = \frac{0.43(mGTE_r + (\xi TE_r)^2 + \sigma_{0t}^2)^{1/2}}{TE_r}$$

$$\sigma_A = 0.43\left(\frac{mG}{TE_r} + \xi^2 + \frac{\sigma_{0t}^2}{TE_r^{\,2}}\right)^{1/2}$$

$(\sigma_A)_{sh} \ \alpha \ 1/\sqrt{T}$ → Shot noise limited

$(\sigma_A)_{fl} \ \alpha$ Constant → Flicker noise limited

$(\sigma_A)_{0t} \ \alpha \ 1/T$ → Zero transmittance noise limited

Example;

1)
- $\overline{T_1}=0.8$ $\sigma A1=0.02$
- $\overline{T_2}=0.4$ $\sigma A2=0.02$

In this case flicker noise is dominant

2)
- $T_1=0.8$ $\sigma A1=0.04$
- $T2=0.4$ $\sigma A2=0.08$

Zero transmittance current Is limiting

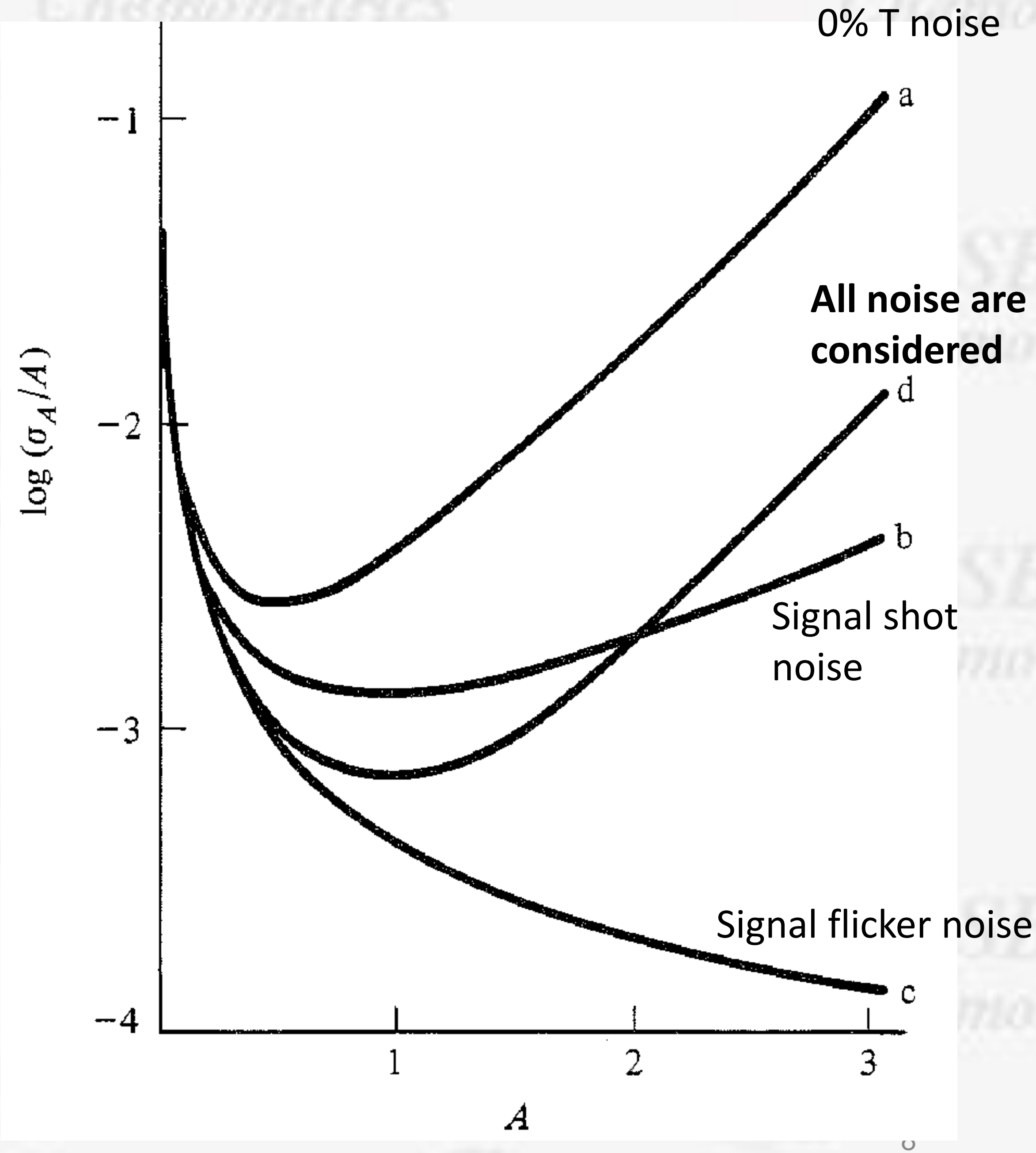
Noise to signal diagram;

$$\sigma_A = 0.43\frac{\sigma_{st}}{TE_r} = 0.43\frac{\sigma_{st}}{E_s}$$

$$\frac{\sigma_A}{A} = \frac{\sigma_A}{-lnT} = 0.43\frac{\sigma_{st}}{-TE_r lnT}$$

$$\sigma_{st} = (mGE_s + (\xi E_s)^2 + \sigma_{0t}^2)^{1/2}$$

$$\frac{\sigma_A}{A} = 0.43\left(\frac{mG}{TE_rA^2} + \frac{\xi^2}{A^2} + \frac{\sigma_{0t}^2}{(TE_rA)^2}\right)^{1/2}$$



Zero Transmittance (0%) Noise limited

When analyte concentration is very high and T is considerably low
-or when detector noise is high (IR detectors)

$$\frac{\sigma_A}{A} = 0.43\left(\cancel{\frac{mG}{TE_rA^2}} + \cancel{\frac{\xi^2}{A^2}} + \frac{\sigma_{0t}^2}{(TE_rA)^2}\right)^{1/2}$$

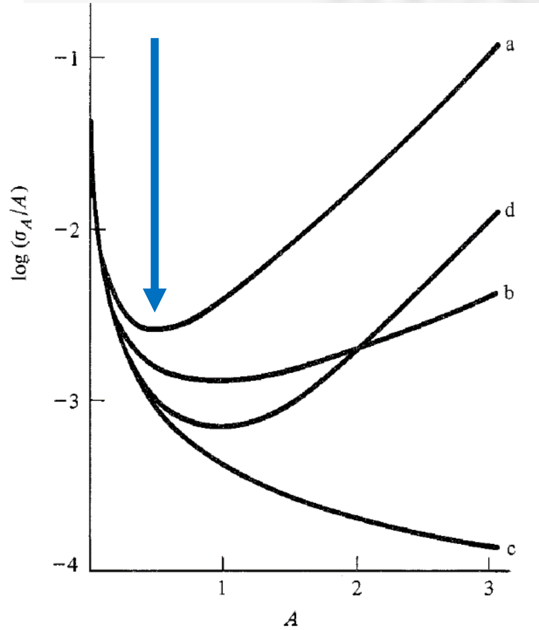
$$\sigma_{0t} = (\sigma_d^2 + \sigma_{ar}^2 + \sigma_{bE}^2)^{1/2}$$

$$\sigma_{0t} = [(\sigma_{bE})_s^2 + (\sigma_{bE})_f^2 + (\sigma_d)_s^2 + \sigma_{ar}^2 + (\sigma_d)_{ex}^2]^{1/2}$$

$$\frac{\sigma_A}{A} = \frac{\sigma_{0t}}{-E_rT\ln T} = \frac{\sigma_{0t}}{-E_{fs}T\ln T}$$

Differentition =0

→ min A=0.434 min σA/A



- Intensive source
- Wider slit → E_r ↑ → σA/A↓

- (Sample absorb ↓) T↑

Signal Shot noise limited

$$\frac{\sigma_A}{A} = 0.43\left(\frac{mG}{TE_rA^2} + \cancel{\frac{\xi^2}{A^2}} + \cancel{\frac{\sigma_0^2 t}{(TE_rA)^2}}\right)^{1/2}$$

$$\frac{\sigma_A}{A} = \frac{[mGK/(TE_r)]^{1/2}}{-\ln T} = \frac{(K/Ti_r)^{1/2}}{-\ln T}$$

-integration time↑

→ Δf↓ → K↓ → σA/A↓

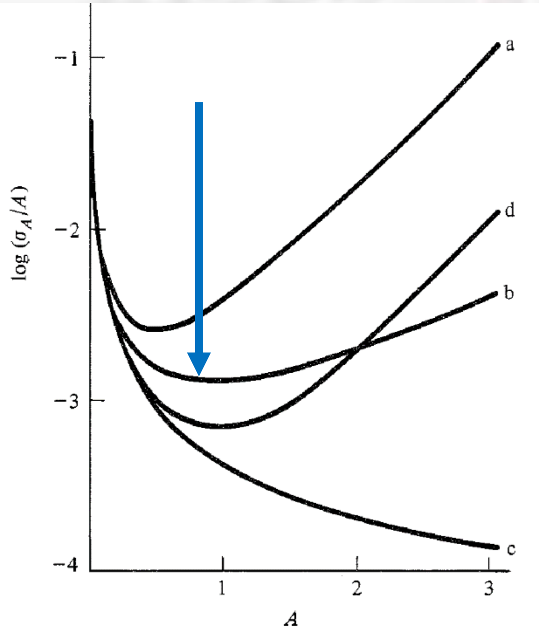
-Intensive source

-Wider slit → i_r ↑

-T↑ → i_s ↑

derivative =0

→ A=0.87 min σA/A



Signal-Flicker noise limited

$$\frac{\sigma_A}{A} = 0.43\left(\cancel{\frac{mG}{TE_rA^2}} + \frac{\xi^2}{A^2} + \cancel{\frac{\sigma_0^2 t}{(TE_rA)^2}}\right)^{1/2}$$

$$\xi_s = (\xi_1^2 + \xi_2^2)^{1/2}$$

Source flicker factor (ξ_1)

Container flicker factor (ξ_2)

$$\frac{\sigma_A}{A} = \frac{\xi_s}{-\ln T} = \frac{\xi_s}{A}$$

$$\sigma_A = \xi_s$$

$\xi \downarrow \Rightarrow$ S/N$\uparrow$

-More Stable light source.

-Double beam