Limiting Noise

$i_t = i_s + i_{bg} + i_d$

$\sigma_t = (\sigma_s^2 + \sigma_{bg}^2 + \sigma_d^2)^{1/2}$

Emission and Luminescence:

- $\sigma_t \approx \sigma_{bk}$: Blank noise limited
  - $\sigma_{bk} >> \sigma_{dt}$ (Background noise limited)
  - $\sigma_{bk} \approx \sigma_{dt}$ (Dark total noise limited)
- $\sigma_t >> \sigma_{bk}$: Analytical Signal noise limited
  - $\sigma_S \propto (i)^{1/2}$ (Signal shot noise limited)
  - $\sigma_S \propto i$ (Signal flicker noise limited)

Transmittance:

if $\sigma_s \propto (T)^{1/2}$

if $\sigma_f \propto T$

if $\sigma_{ot} \propto$ const

Analyte concn↑ → T↓↓ → σ_{ot} limited

Analyte concn↓ → T↑↑ → σ_s or σ_f limited

$i_{st} = i_s + i_{ot}$

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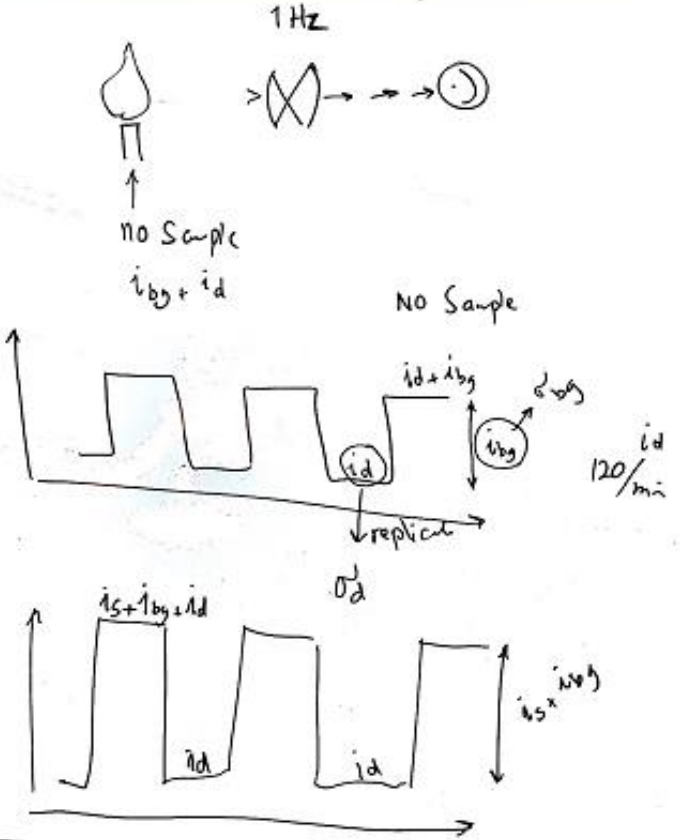
بنام خدا

S/N ratio enhancement

Emission and/or fluorescence:

Source intensity ↑ ⟶ fluorec. ↑ Φ

$i_{tot} = i_F + \underbrace{i_{bg} + i_{dark}}_{i_{bn}}$

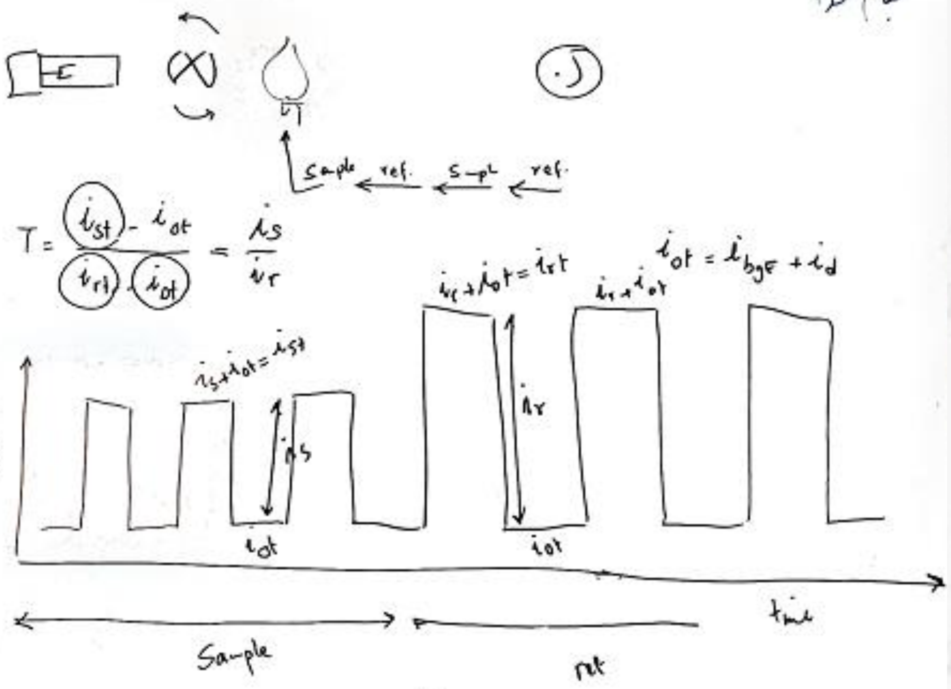


Absorbance:

$$T = \frac{E_{st} - E_{ot}}{E_{rt} - E_{ot}} \qquad i_{st} = i_s + i_{ot}$$

$A = -\log T$

Chopp off: $i_d = i_{ot}$



$$T = \frac{i_{st} - i_{ot}}{i_{rt} - i_{ot}} = \frac{i_s}{i_r}$$

$i_{ot} = i_{bgr} + i_d$

Smoothing:

(Chopper 50 Hz)

modulation ⟶ 100 Hz signal $\xrightarrow{\text{filter}}$

5-6 S/N ratio enhancement techniques:

I.

AC or DC signal + Integration and **smoothing** → S/N↑
AC signal + band pass **filter** and lock in amplifier →

II.

i_B ↓ → S/B ↑ → S/N ↑

III. Photon counting:

Emission and Luminescence:

$S/N = ns / \{n_s + n_B + n_d + (\xi n_s)^2 + (\chi n_B)^2\}^{1/2}$

Amplifier readout and excess dark are not included

Absorbance:

$$\frac{\sigma_A}{A} = (n_r \ln T)^{-1}\left[n_r T^{-1} + (n_r \xi_s)^2 + \frac{n_{bE}}{T^2} + \left(\frac{n_{bE}\chi}{T}\right)^2 + \frac{n_d}{T^2}\right]^{1/2}$$

Photon counting (digital) condition is preferred to Analog.

Additional noise:

(Independent of analyte signal)

- Detector Noise
- Amplifier readout noise
- Background Noise.

Multiplicative Noise

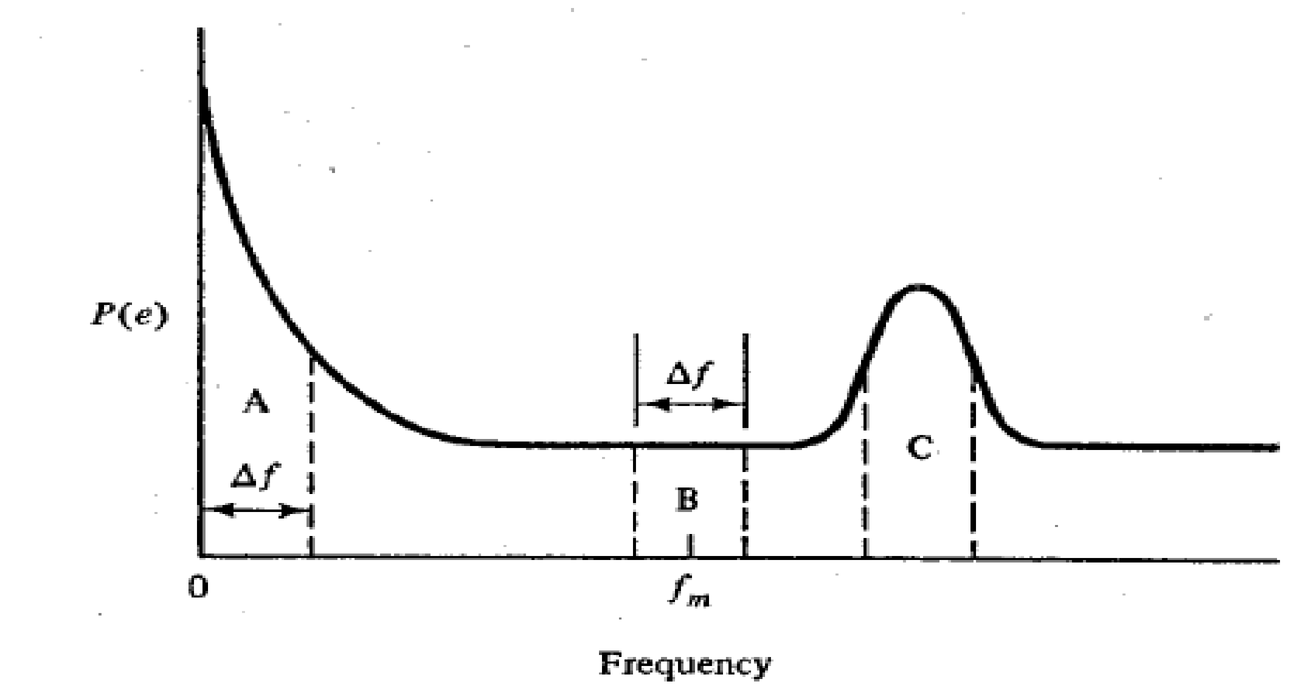
(Dependent on analyte signal)

- Analyte signal shot noise $\propto (i)^{1/2}$
- Analyte signal flicker noise $\propto i$

IV. Modulation:

Modulation can be used to change the frequency, (noise power spectrum)

Modulation encodes the signal information at the modulation frequency (ƒm), region (B).



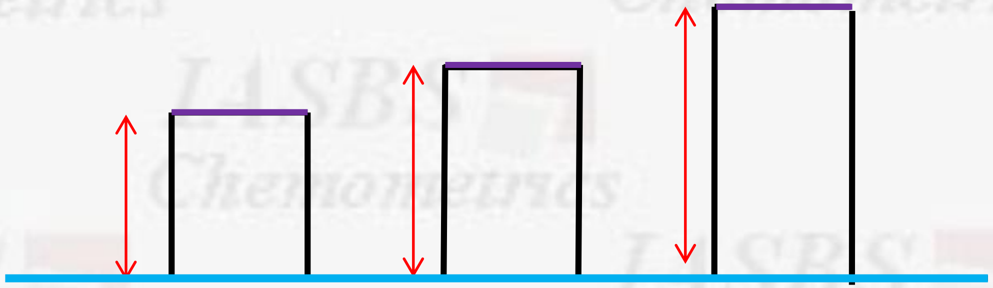
IV. Modulation:

Carried Signal and noise:

Only during one cycle

Ex: Multiplicative

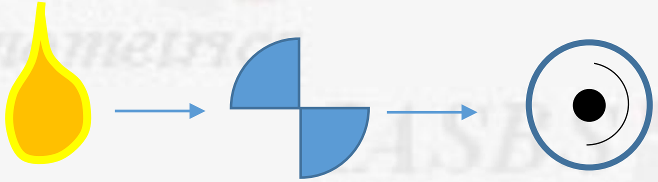
Ex: Additive



Not carried

During on and off cycles

Ex: Addittive:Background signal and noise



Modulation → S/N ↑

If additive noise: not carried.

Ex: Emission Spectroscopy

+ Sample modul

→ Not carried background

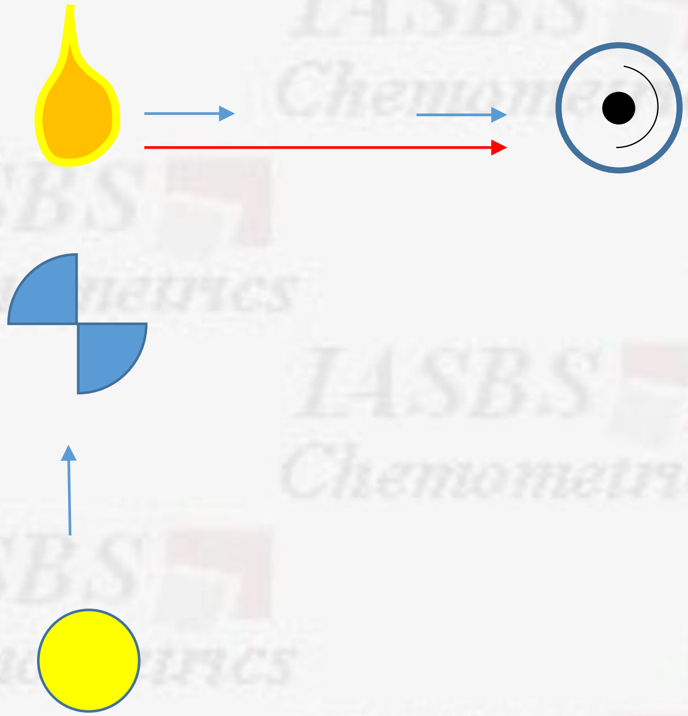
If additive or multiplicative noise is carried S/N does not improve

Ex: Em Spectr + source modulation

→ carried backgr emission signal

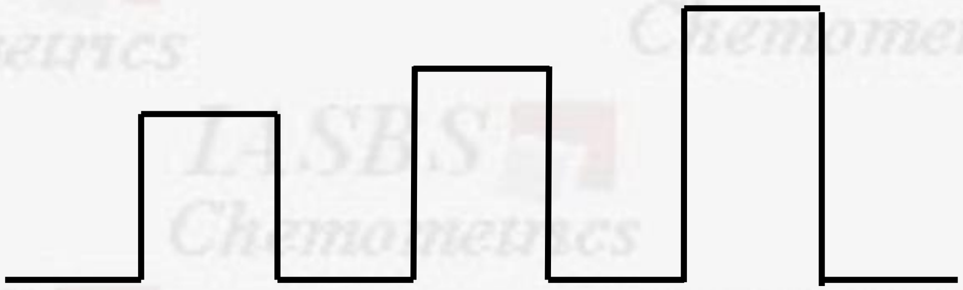
→ no S/N improvement

Atomic Fluorescence +source modulation



-Analyte emission: Not carried.
- Backgr Emiss: Not Carried
- 1/f of source: Carried
- 1/f of flame: Not Carried
- Analyte luminesce: Carried
- Backgr luminesce: Carried
- Scattering: Carried

DC source + chopper
Laser + Q-switch
(peak power= 100x DC power)



+ demodulation

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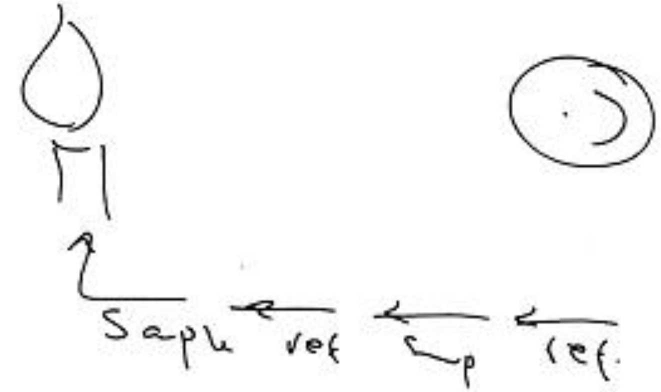
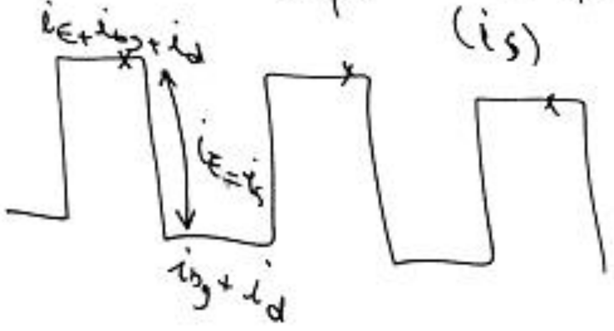


Saple ref Sapl

$i_t = i_E + i_{bg} + i_d$
(i_s)



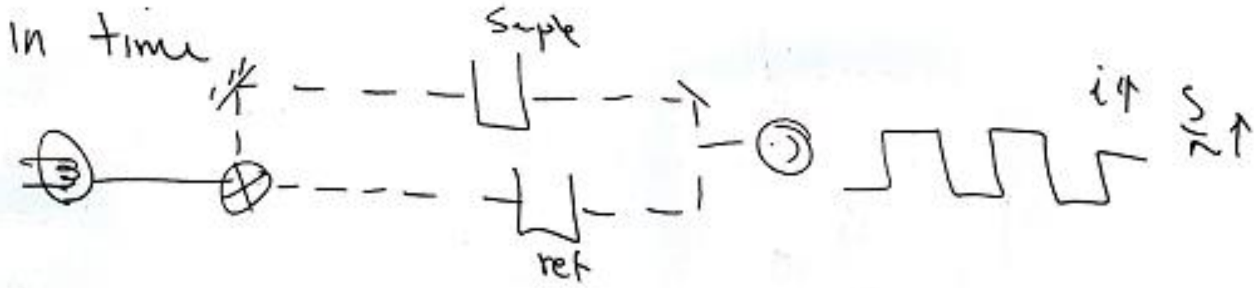
Noncarried: $i_d + i_{bg}$ (DC)

Carrie. : $i_E \equiv i_s$ (AC)

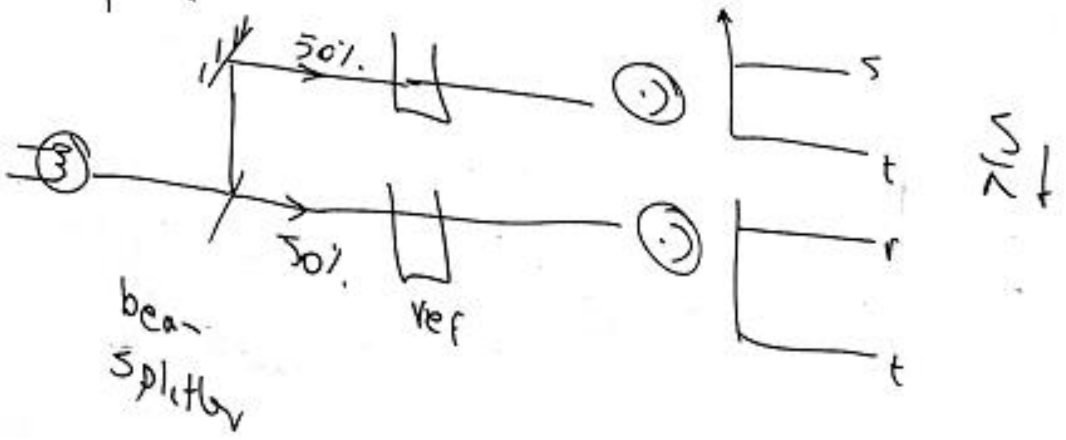
Double beam:

Same condition for ref and Sample.

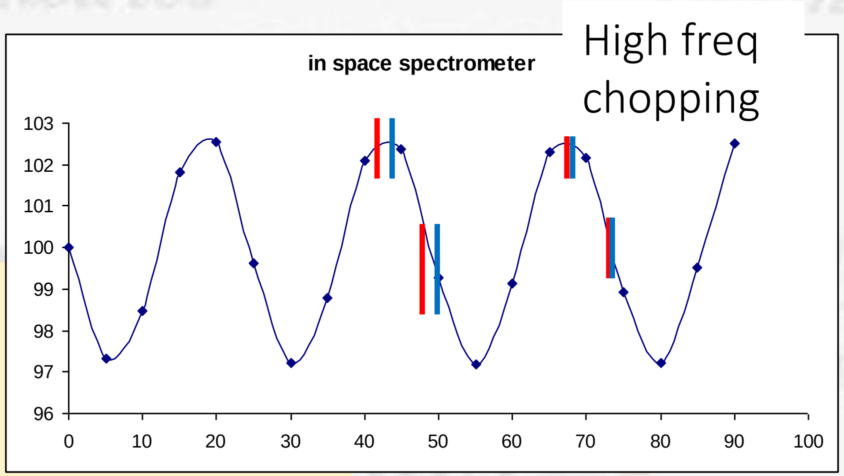
In time



In space



V. Double beam spectrometer.



Reference
Sample

- In time (chopping);

Should be: freq chopper>>flicker noise

→ Elimination of 1/f and interference noise(if frequency< chopper freq)

of flicker noise (if frequency< chopper freq)

- In Space (dual channel):

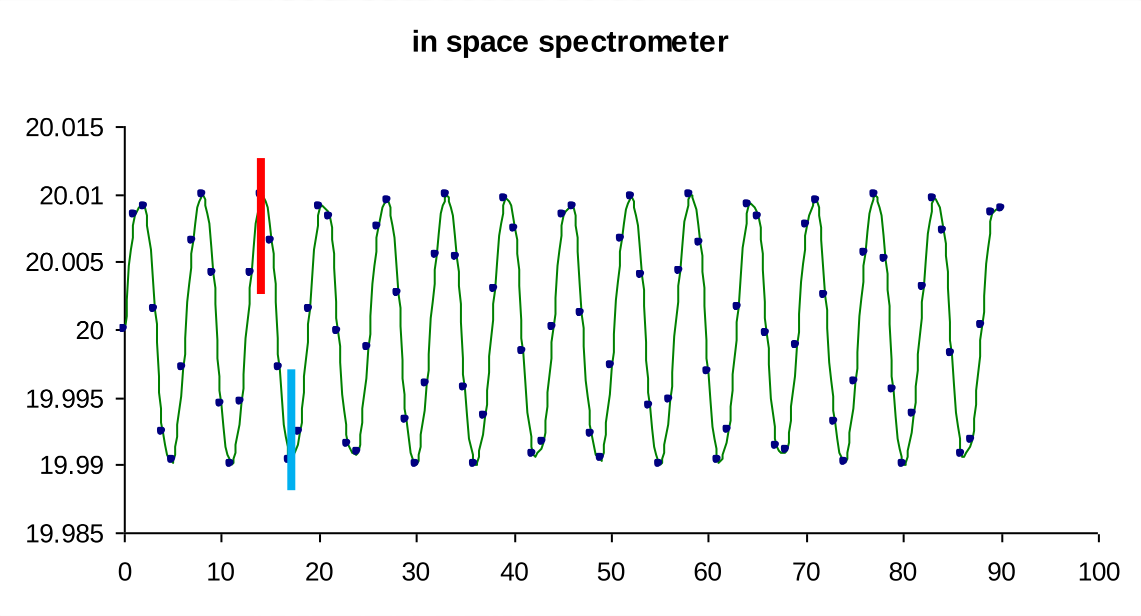
→ Elimination of 1/f and interference noise(any frequency)

of flicker noise (any frequency)

But: i_s↓ → S/N↓

Ex:
is it possible to eliminate an interference noise of 50Hz using a chopping with 30Hz?

4-2) *In space; freq flicker>>freq chapper*



VI. Time domain filtering:

Boxcar integrator (in assigned time interval and periode)

if $S/N \propto (n)^{1/2}$

then: integration improves S/N

(reduces the shot noise effect)

Drift should not be exist during integration

(high frequency of signal acquisition),.

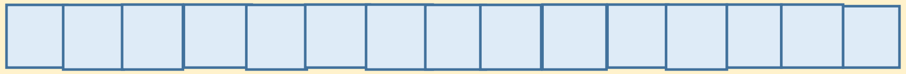
Number of scan of electrode charges in photodiode array in a assigned periode of time, is a meaning of integration.

Digital filtering: Fourier transform (time domain, frequency domain)

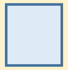
Smoothing (Savitsky-Golay) → $\Delta f \downarrow$

(Moving window, Weighted average)

VII. Multichannel and Multiplexing



15 wavelengths by 15 channels



15 wavelengths by 1 channels

Multichannel and single channel:
Same spectrum in fixed time t for both
→ # photons observed per spectral resolution element is n times greater for multichannel detector.
→ $(S/N)_{MultiCh} = n^{1/2} (S/N)_{SingCh}$
(if shot n. limited)

(n: number of spectral resolution elements)

Multiplex systems:
(if shot noise limited)

Michaelson interferometer
n time measuring interferogram
+ FT → n spectra in time t

→ $(S/N)_m = m^{1/2} (S/N)_1$

VIII. High throughput

- Michaelson interferometer.
- Dispersion to lower solid angle, and high slit width.

    high responsivity of detector (not m)
    lower detector noise

Interferance;
- Blank interferance,
- Analyte interferance

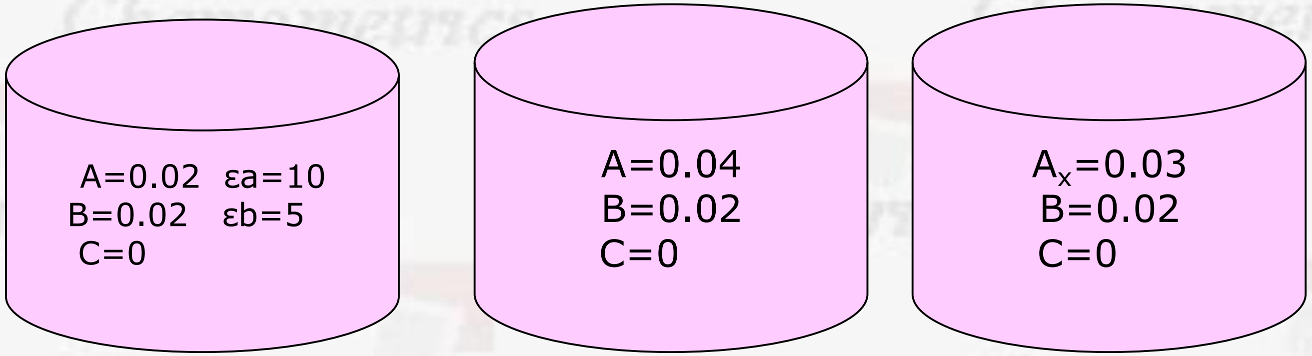
interferance
- spectral
- Non spectral

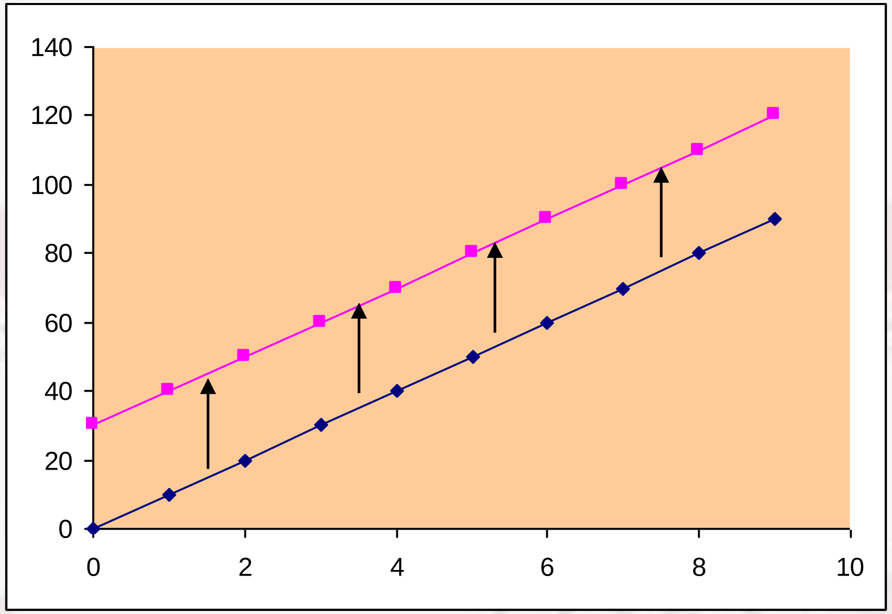
Blank spectral interferance;

A=analyte

B=blank

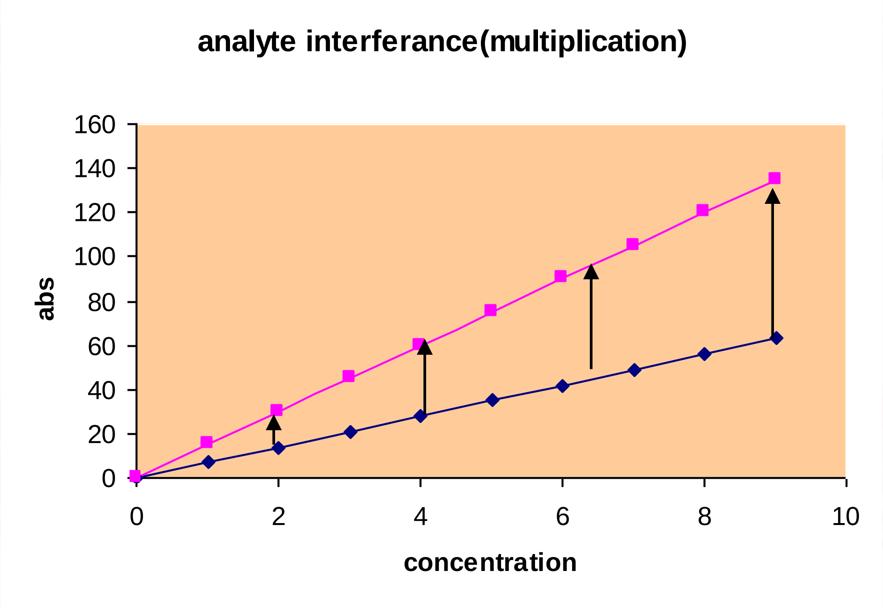
C=interferance





Additive interferance

Analyte interferance;



Non spectral analyte interferance

Such as matrix effect cause error

Correspand to concentration of analyte.