

# THREE COMPONENTS OF CHEMICAL SENSING

- recognition
- amplification
- data reduction to information

QuickTime™ and a  
TIFF (LZW) decompressor  
are needed to see this picture.

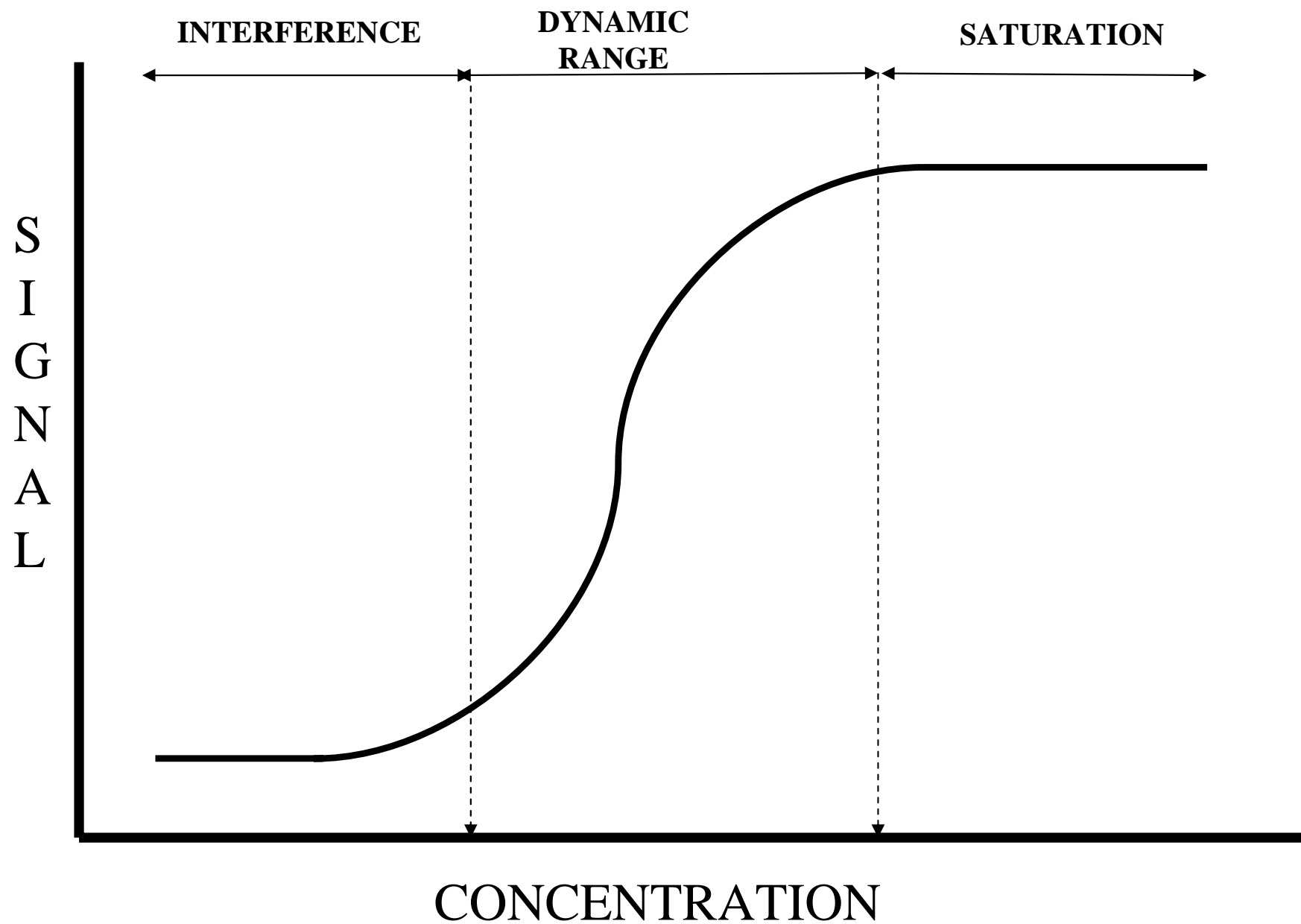
# FIGURES OF MERIT

Selectivity  
Detection limit  
Sensitivity  
Reversibility  
Ruggedness  
Response time  
Cost

Q: WHICH SENSOR IS THE BEST?

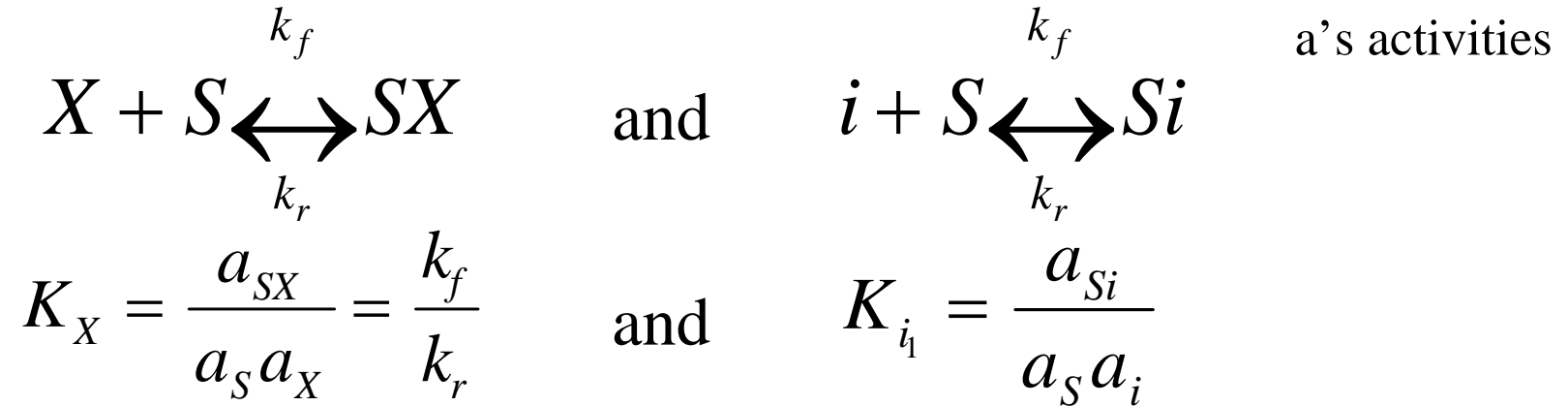
A: WHICHEVER FITS BEST THE APPLICATION

# RESPONSE CURVE



# THERMODYNAMICS OF INTERACTIONS

- selective layer contains specific *binding sites*  $S$  which are in equilibrium with *analyte*  $X$  and with *interferant*  $i$



- selective layer can be *homogeneous* or *heterogeneous*
- free energy of interaction is

$$0 = \Delta G = \Delta G^0 + RT \ln \frac{a_{SX}}{a_S a_X}$$

- for  $K > 10^4$  or  $\Delta G > 23 \text{ kJ mol}^{-1}$  interaction is irreversible

# OCCUPATION OF BINDING SITES

- total activity of binding sites is

$$a_{ST} = a_{SX} + a_{Si} + a_S$$

- activity of occupied binding sites giving rise to the signal is

$$a_O = a_{SX} + \sum_i a_{Si}$$

- for signal from all occupied sites is then

$$a_O = a_{ST} \frac{a_X + \sum_i K'_i a_i}{a_X + \sum_i K'_i a_i + 1/K_X}$$

in which constant  $K'$  has meaning of *selectivity coefficient*

$$K'_i = K_i / K_X$$

# RESPONSE CURVE REGIONS

REGION I: **SATURATION**

$$a_X \gg (\sum K_i a_i + 1/K')$$

$$a_O = a_{ST}$$

$$a_O = a_{ST} \frac{a_X + \sum_i K_i' a_i}{a_X + \sum_i K_i' a_i + 1/K_X}$$

REGION II: **DYNAMIC RANGE**

$$\sum_i K_i' a_i \ll a_X \ll 1/K_X$$

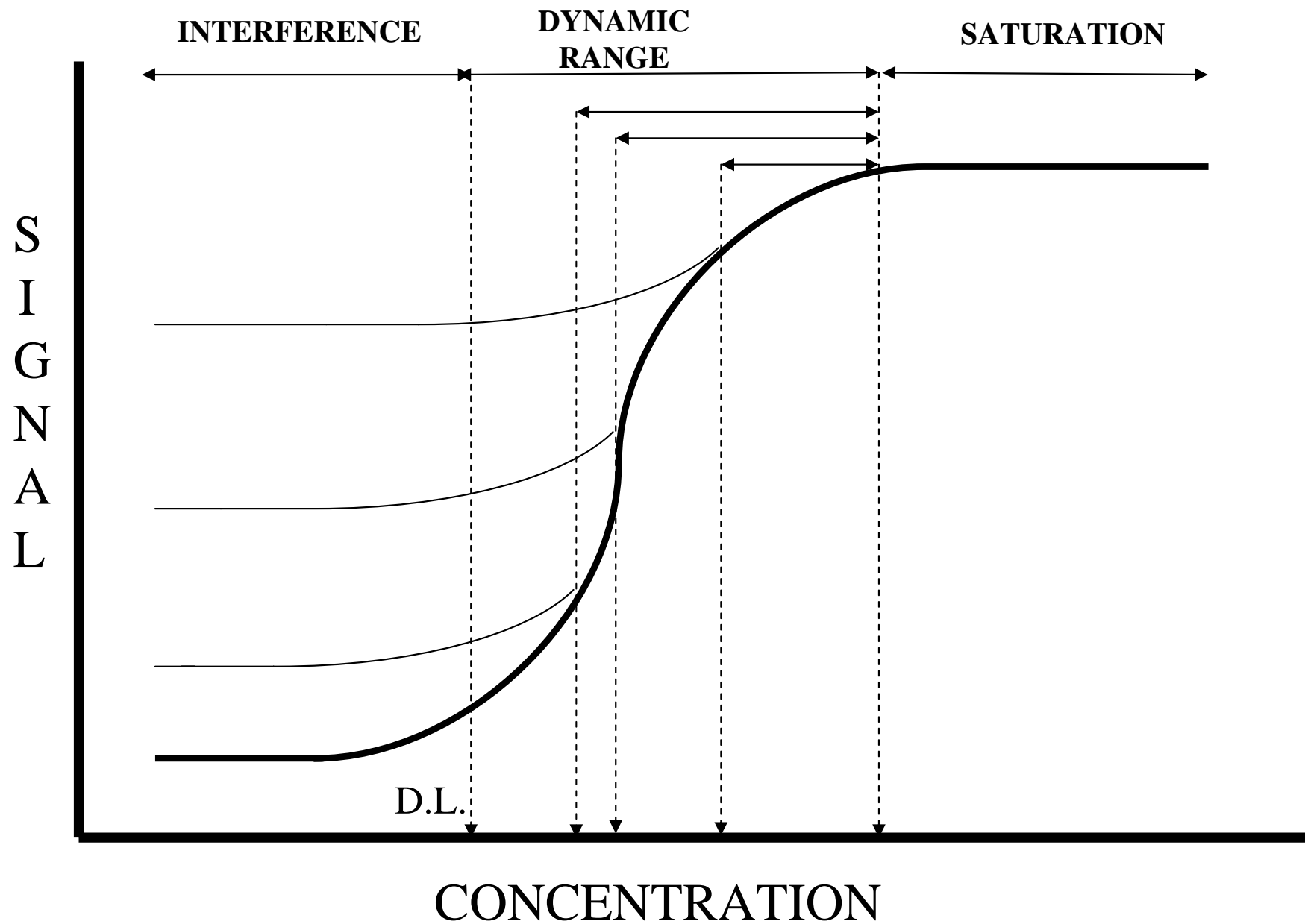
$$a_O = a_{ST} K_X a_X$$

REGION III: **INTERFERENCE RANGE**

$$a_X \ll \sum_i K_i' a_i + 1/K_X$$

$$a_O = a_{ST} \sum_i K_i a_i$$

# EFFECT OF INTERFERENCES



# DETECTION LIMIT

- Intercept of dynamic range and interference range defines detection limit

$$(a_X)_{d.l.} = \frac{\sum_i K'_i a_i}{\sum_i K_i a_i + 1}$$

or

$$K'_i = K_i / K_X = \frac{(a_X)_{d.l.}}{a_i}$$

- Dynamic range is difference between saturation and detection limits

$$D.R. = (a_X)_{s.l.} - (a_X)_{d.l.} = \frac{1}{K_X} - K'_i a_i$$

- As concentration of interferants increases dynamic range becomes narrower until it vanishes. All sites are now occupied by the Interferant.

# BULK OR SURFACE INTERACTIONS?

- BULK INTERACTIONS ARE DEFINED BY THE EQUALITY OF CHEMICAL POTENTIALS BETWEEN THE SELECTIVE LAYER AND THE SAMPLE.

$$(\mu_x)_{sensor} = (\mu_x)_{sample}$$

IT YIELDS *LOGARITHMIC RESPONSE*

$$\mu_x = \mu_x^0 + \Re T \ln a_x$$

- THE EQUALITY OF CHEMICAL POTENTIALS OF ADSORBED SPECIES AND SAMPLE LEAD TO VARIOUS *ADSORPTION ISOTHERMS*

# THEORETICAL DYNAMIC RANGE

- RESPONSE RELATED TO OCCUPIED SITES BY  $E_{\text{out}} = \mathfrak{R}_f(a_O)$
- SINGLE BINDING SITE YIELDS 5 DECADES
- MULTIPLE BINDING SITES YIELD WIDE DYNAMIC RANGE

$$a_{\text{SX}} = a_X(K_1 a_{\text{T},1} + K_2 a_{\text{T},2} + \dots + K_n a_{\text{T},n})$$

OR

$$E_{\text{out}} = \mathfrak{R}_f a_X (K_1 a_{\text{T},1} + K_2 a_{\text{T},2} + \dots + K_n a_{\text{T},n})$$

EXAMPLE: DYNAMIC RANGE OF GLASS ELECTRODE IS 36 DECADES!!

# ACTIVITY OR CONCENTRATION

- CONSIDER SENSORS RESPONDING TO *GRADIENT* OR *RATE OF CHANGE*

$$E_{out} = \Re(\sum_i K_i \frac{dC_i}{dx}) \quad \text{OR} \quad E_{out} = \Re(\sum_i K_i \frac{dC_i}{dt})$$

$$a = f C$$

Differentiate:

because

$$\frac{da}{dx} = \frac{df}{dx} C + f \frac{dC}{dx} \approx f \frac{dC}{dx} \quad \frac{df}{dx} = \frac{df}{dt} = 0$$

$$\frac{da}{dt} = \frac{df}{dt} C + f \frac{dC}{dt} \approx f \frac{dC}{dt}$$