

Types of calibration methods:

External Calibration

- Signal is proportional to concentration - established using externally prepared standards
- Assumes that the sensitivity (signal/conc) is the same for samples and standards
- Assumes that the signal arises only from the analyte in most cases
- Does not account for **sample matrix** or **instrumental drift**

Standard Addition

- Known amounts of analyte are added to aliquots of sample
- Signals are measured as a function of concentration added
- Accounts for **sample matrix**, but not for **instrumental drift**

Internal Standard

- A substance known as an “internal standard” is added to samples and standards (chemically similar to analyte)
- Used to correct for **drift** (changes in sensitivity over time) and **matrix effects** (sample-related changes in sensitivity)

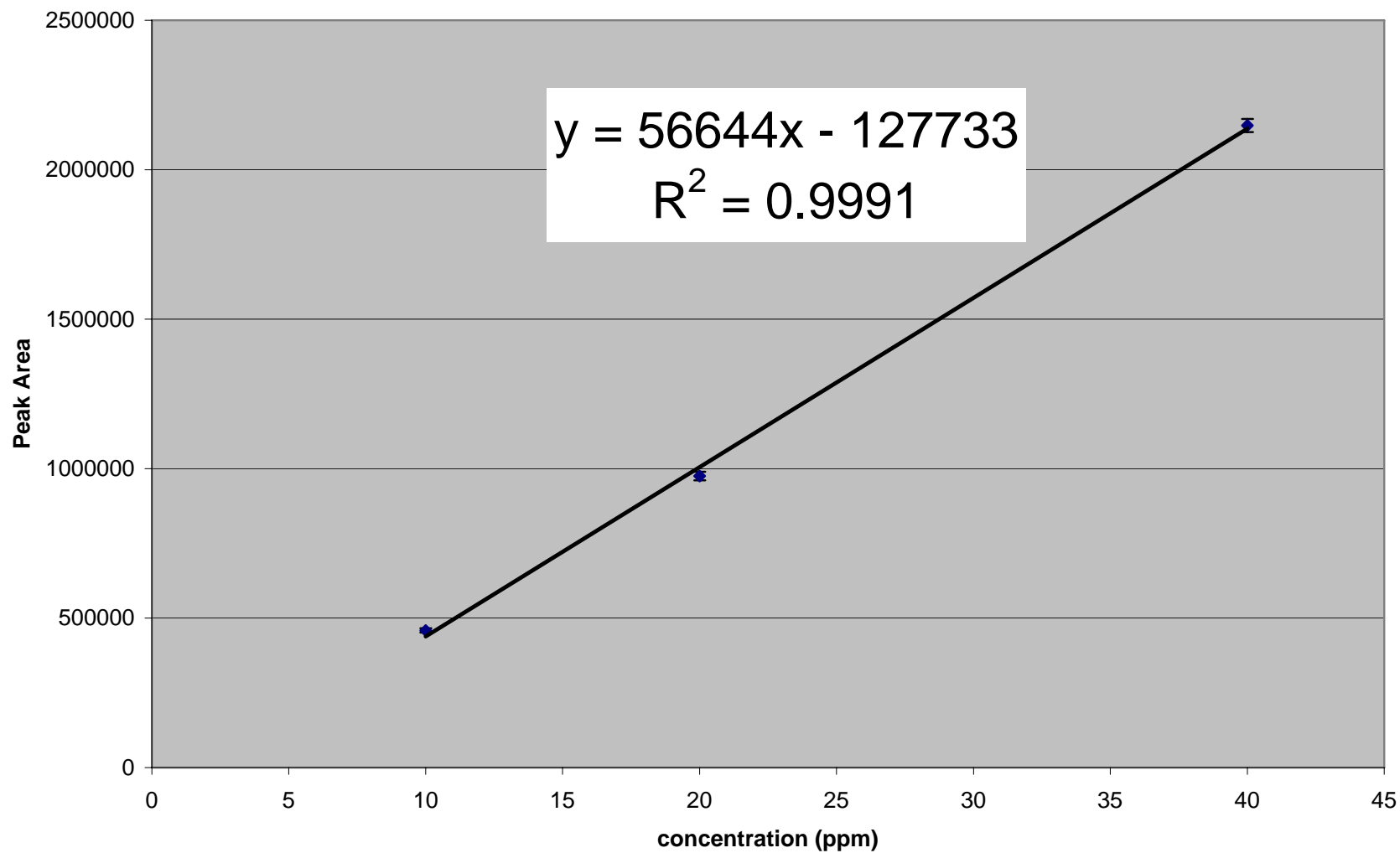
External Calibration – Standards of sulfate used at 10, 20, and 40 ppm

Exercise 1

Determine average peak area, standard deviation of measurement (from 3 data points), and graph concentration (ppm) vs. the average peak area - include error bars (std dev)
Sulfate data (collected by Ion Chromatography)

	Run 1	Run 2	Run 3
Conc (ppm)	Peak area	Peak area	Peak area
10	466593	459525	449252
20	985270	986335	954947
40	2162970	2163860	2116861

Conc (ppm)	Run 1 Peak area	Run 2 Peak area	Run 3 Peak area	ave	std dev
10	466593	459525	449252	458456.6667	7119.6242
20	985270	986335	954947	975517.3333	14551.919
40	2162970	2163860	2116861	2147897	21948.774



Exercise 2

Determine concentration of sulfate from water samples using calibration data from Exercise 1. Plot data as bar graph (sample vs. undil conc in ppm)

Sample	Peak area	ppm diluted conc.	dilution factor	ppm undiluted concentration
Box Canyon Well #1	1085116		1:7	
Box Canyon Trough Running	1187024		1:7	
Box Canyon Trough still	1287262		1:7	
Windmill Trough Still	191852		1:51	
Windmill Trough Running	329316		1:26	
Tohatchi Spring	234947		1:26	
Balokai Well Trough	543660		1:26	
Balokai Well	524457		1:26	

How do you take a calibration and use it to determine concentrations of samples?

Recall: least square's fit of calibration data

$$y = 56644x - 127733$$

$$R^2 = 0.9991$$

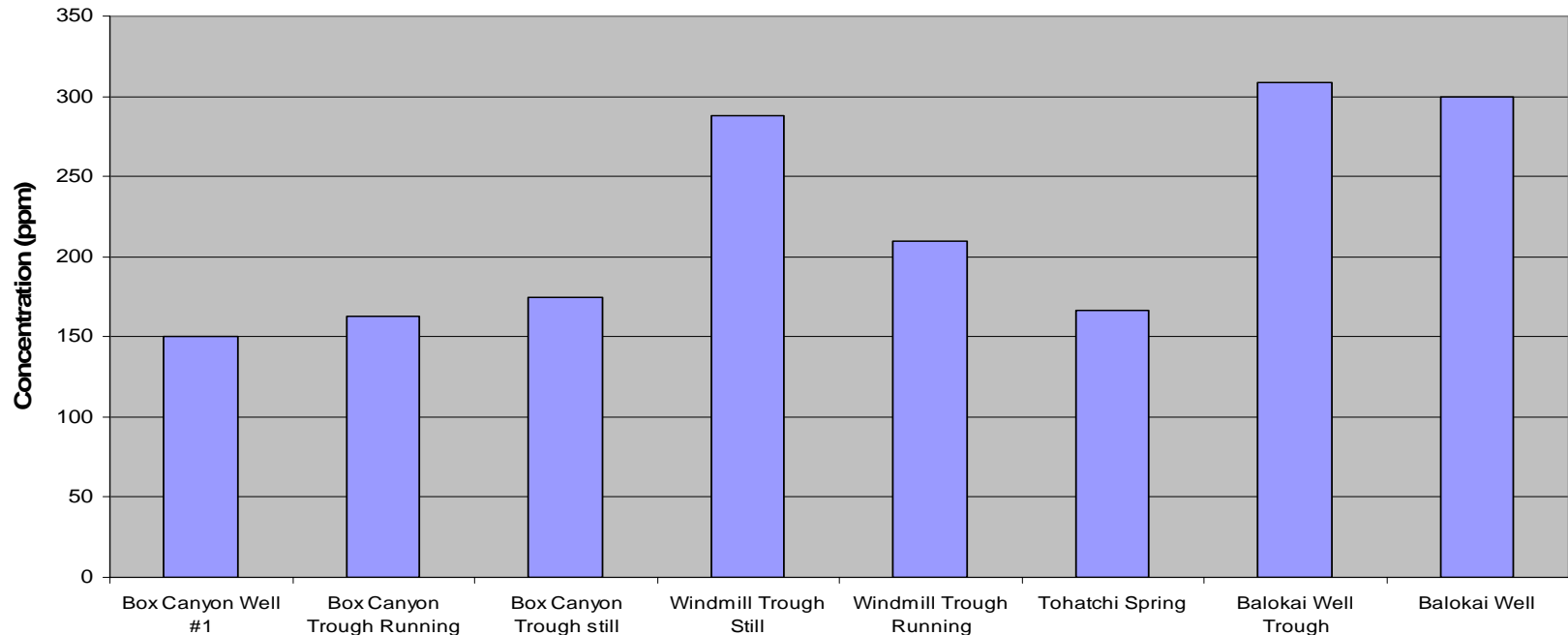
*Where y is the peak area (measured signal)
and x is the concentration (ppm)*

For the samples, we measured the peak area using ion chromatography. We use the line equation of the least square's fit to calculate the concentrations:

$$\mathbf{x = (y + 127733) / 56644}$$

Determine concentration of sulfate from water samples using calibration data from Exercise 1. Plot data as bar graph (sample vs. undil conc in ppm)

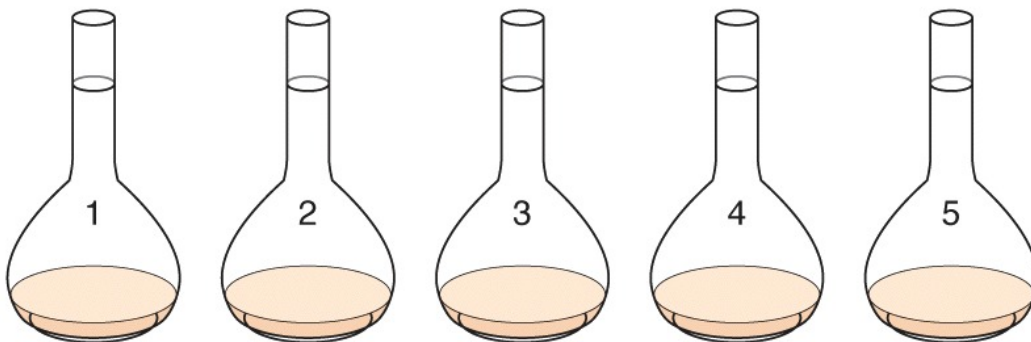
Sample	Peak area	diluted conc.	dilution factor	undiluted concentration
Box Canyon Well #1	1085116	21	1:7	150
Box Canyon Trough Running	1187024	23	1:7	162
Box Canyon Trough still	1287262	25	1:7	175
Windmill Trough Still	191852	6	1:51	288
Windmill Trough Running	329316	8	1:26	210
Tohatchi Spring	234947	6	1:26	166
Balokai Well Trough	543660	12	1:26	308
Balokai Well	524457	12	1:26	299



Standard Addition Calibration

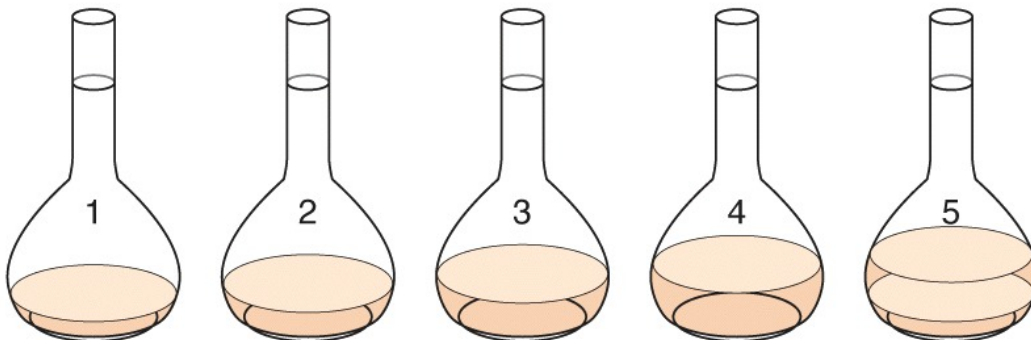
Step 1

Place 5 mL of unknown in each flask



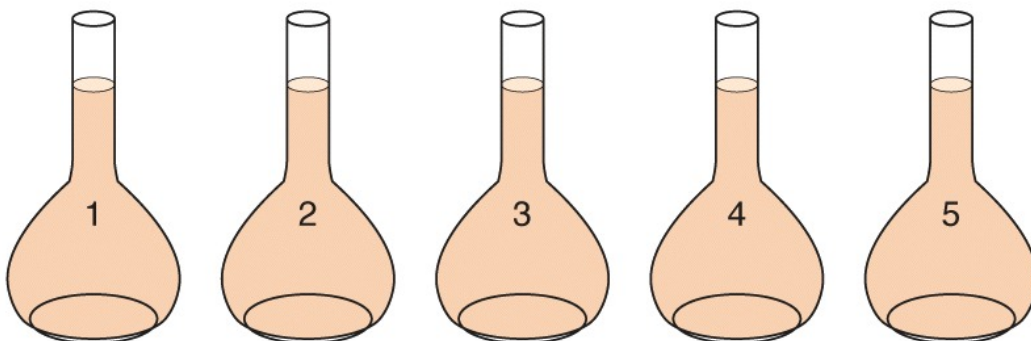
Step 2

Add 0, 5, 10, 15, or 20 mL of standard

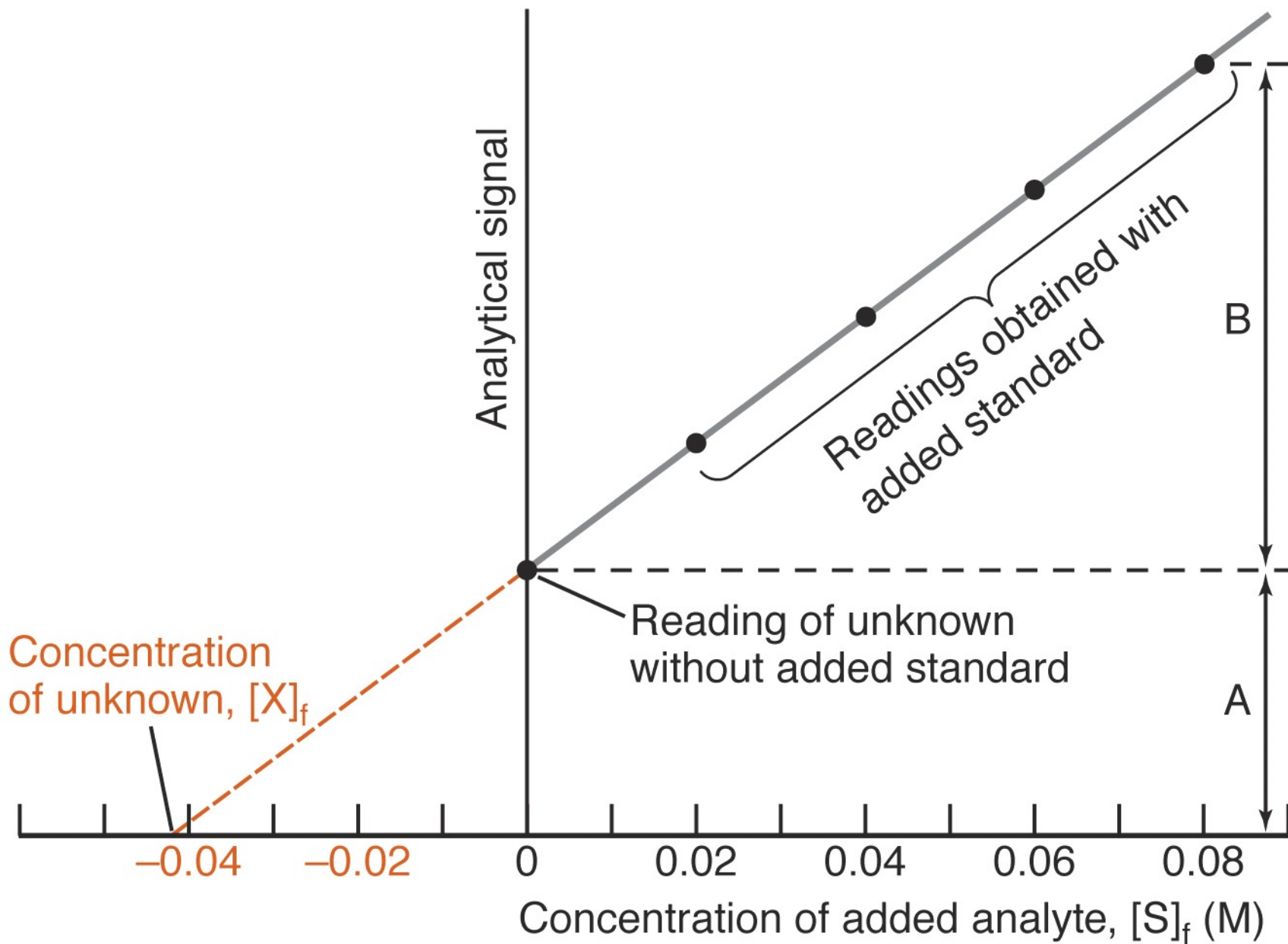


Step 3

Fill each flask to the 50-mL mark and mix



Step 4 - Analyses



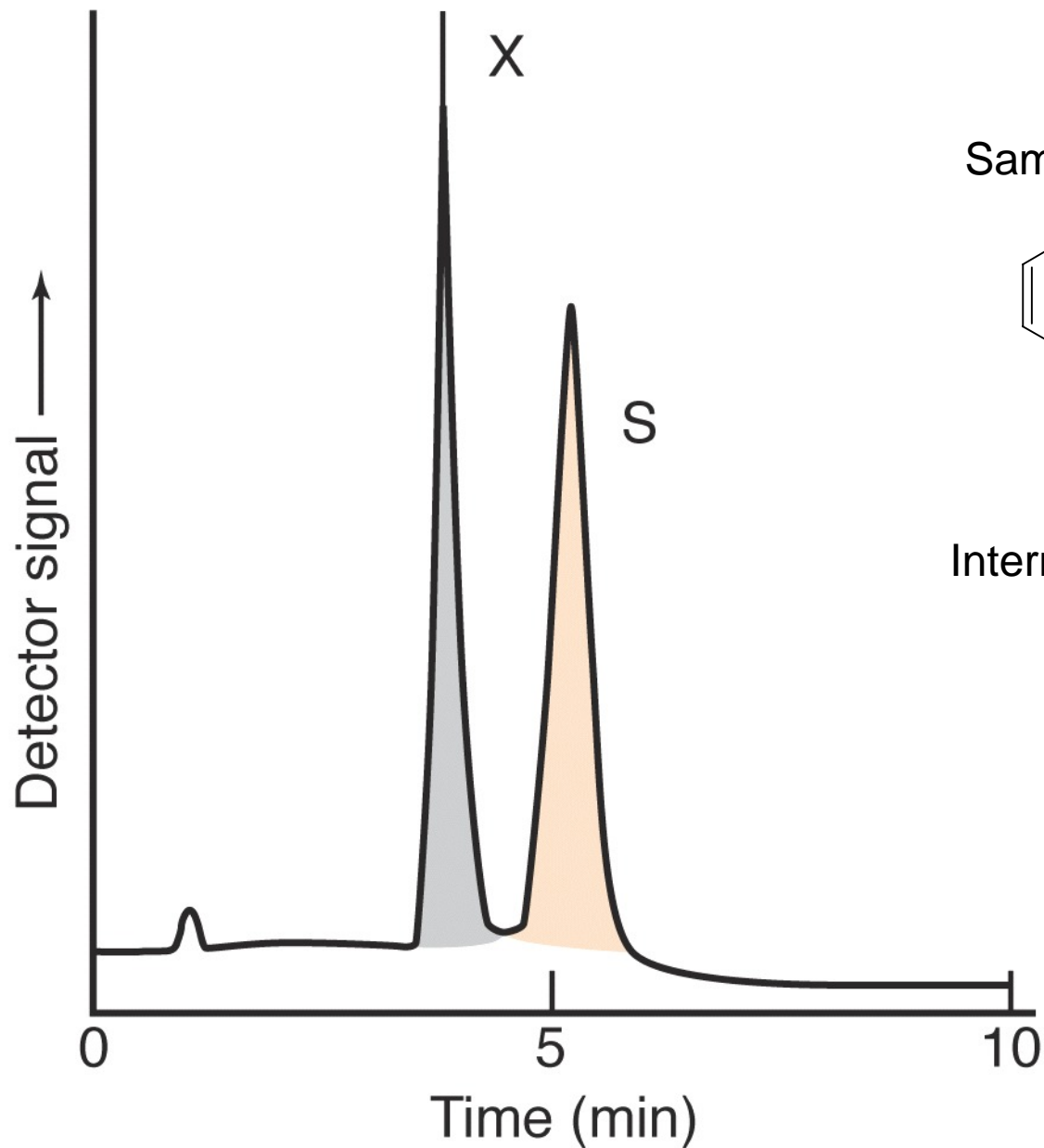
Internal Standard Equation (linear)

$$I_{\text{analyte}} / I_{\text{intstd}} = k * [\text{Analyte}] / [\text{internal std}]$$

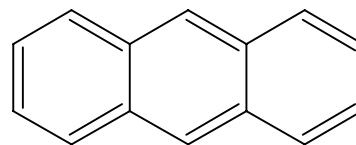
Requirements for an internal standard

- Technique must be multicomponent - must separately measure signals for analyte and internal standard
- No interferences: analyte \rightleftharpoons internal std or sample matrix \rightleftharpoons internal std
- Internal standard must emulate drift and matrix effect behavior
- Internal standard is not native in the sample

Internal Standard Calibration



Sample: Anthracene



Internal Standard: Naphthalene

