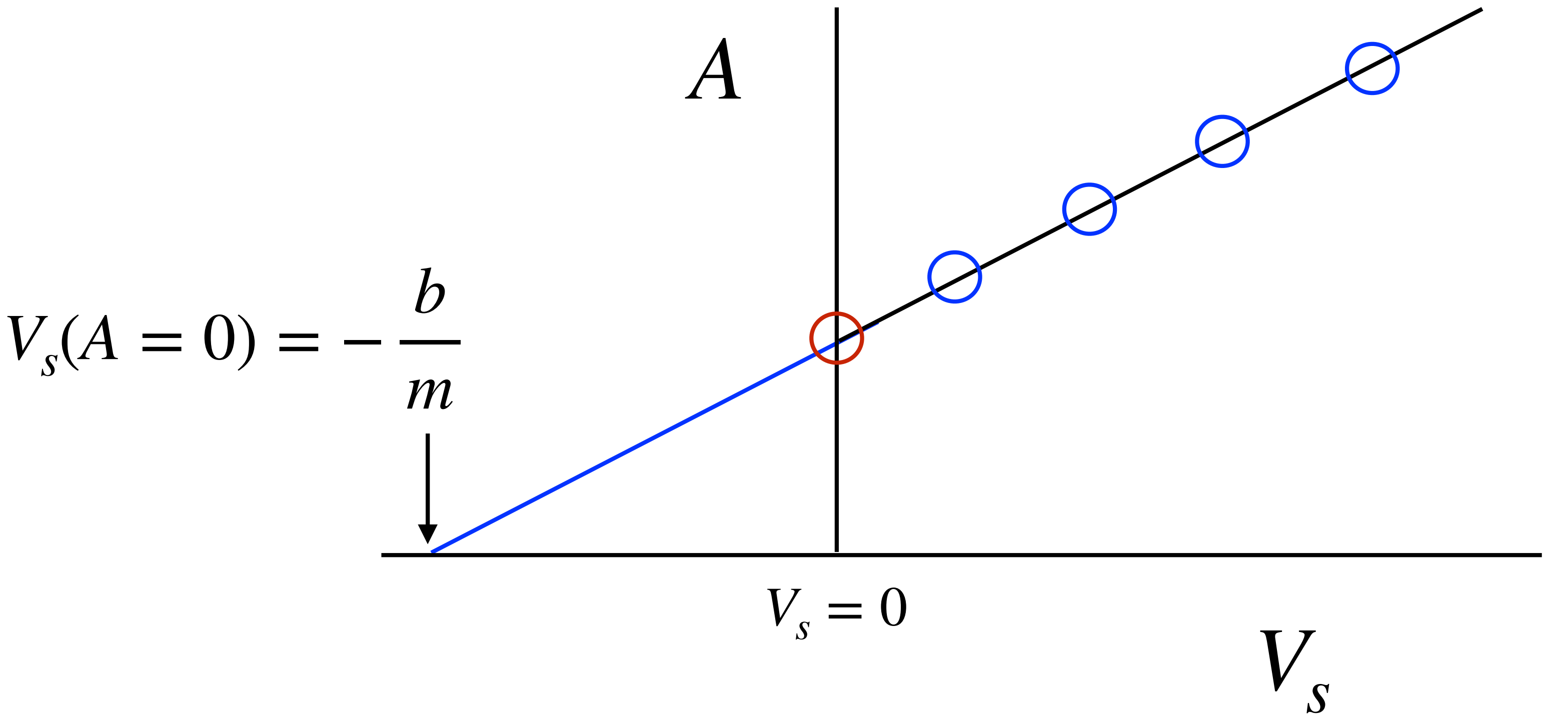
Method of Standard Addition



$$A = \epsilon d \left(\frac{C_x V_x}{V_t} + \frac{C_s V_s}{V_t} \right) = b + mV_s \longrightarrow C_x = \frac{bC_s}{mVx} = C_s \frac{(b/m)}{Vx}$$

Robert Corn - Chem M3LC
UC Irvine

Method of Standard Addition

You can determine the concentration of an unknown concentration Cx by absorbance (or fluorescence) using the method of standard addition.

To a volumetric flask of volume Vt you:

i) add a volume Vx of the unknown concentration Cx
ii) add a volume Vs of a solution with a known concentration Cs
iii) fill the volumetric to volume Vt

Make five solutions by addition of five different volumes Vs(n) where:

$$V_s(n) = n\Delta \qquad n = 0,1,2,3,4 \qquad \Delta = 5\ mL$$

(for example)

For each solution, the # of moles is CxVx + CsVs and volume is always Vt.
The concentrations of the five solutions are:

$$C_n = \frac{C_x V_x + C_s V_s(n)}{V_t} = \frac{C_x V_x}{V_t} + \frac{C_s n\Delta}{V_t} \qquad n = 0,1,2,3,4$$

Method of Standard Addition

We end up with five solutions of different concentrations Cn:

$$C_n = \frac{C_x V_x + C_s V_s(n)}{V_t} \qquad n = 0,1,2,3,4$$

Measure the Absorbance of each solution A(n):

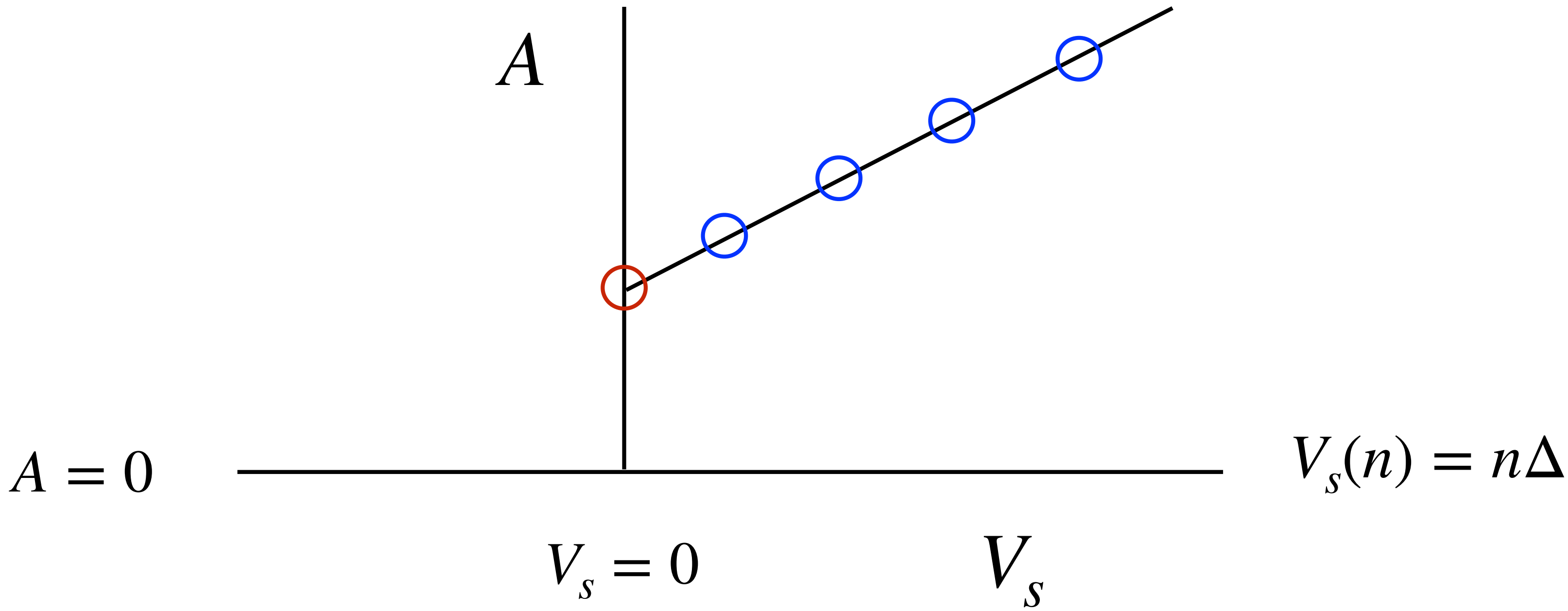
$$A(n) = \epsilon d C_n = \epsilon d \left(\frac{C_x V_x}{V_t} + \frac{C_s V_s(n)}{V_t} \right) = b + m V_s(n)$$

Plot Absorbance vs Vs and fit with a straight line to obtain m & b.

$$\frac{b}{m} = \frac{C_x V_x}{C_s} \longrightarrow \boxed{C_x = C_s \frac{(b/m)}{Vx}}$$

Method of Standard Addition

$$A(n) = b + mV_s(n)$$

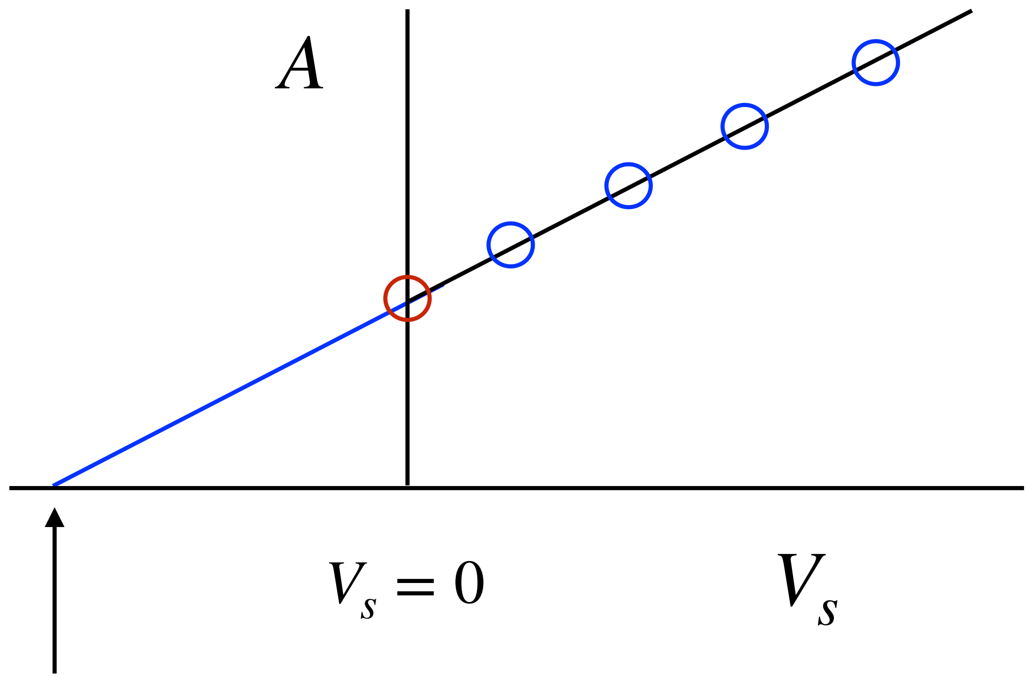


Plot Absorbance vs Vs and fit with a straight line to get a slope and intercept m & b.

$$\frac{b}{m} = \frac{C_x V_x}{C_s} \longrightarrow \boxed{C_x = C_s \frac{(b/m)}{Vx}}$$

Method of Standard Addition

$$A(n) = b + mV_s(n)$$



$$A = 0$$

$$V_s(n) = n\Delta$$

$$V_s(A=0) = -\frac{b}{m}$$

b/m has units of volume

The x intercept at A=0 is -b/m

$$V_s(A=0) = -\frac{b}{m}$$

$$C_x = C_s \frac{(b/m)}{Vx}$$

Method of Standard Addition

$$A = \epsilon d \left(\frac{C_x V_x}{V_t} + \frac{C_s V_s}{V_t} \right) = b + m V_s$$

$$\frac{b}{m} = \frac{C_x V_x}{C_s} \longrightarrow \boxed{C_x = C_s \frac{(b/m)}{Vx}}$$

Standard deviation for Cx is sc:

$$s_c = \frac{C_s}{V_x} \frac{s_r}{m} \sqrt{\frac{1}{N} + \frac{(\bar{y})^2}{m^2 S_{xx}}}$$

Book has different equation because they plot CsVs/Vx instead of Vs. See paper in Other Handouts.

95% confidence interval: $C_x \pm t_{N-2} s_c$

Method of Standard Addition

	A	B	C	D	E	F	G	H	I	J	K	L
1	Standard #	x: Added Vol. (mL)	y: Reading	xi^2	yi^2	xi*yi		N	5		Standard Conc. (ppm)	50
2	1	0	14	0	196	0		xbar	2		Volume Unknown (mL)	5
3	2	1	25	1	625	25		ybar	36.6		Total Volume (mL)	25
4	3	2	37	4	1369	74		Sxx	10			
5	4	3	47	9	2209	141		Syy	1301.2		-x-intercept (mL or ppm)	1.210526316
6	5	4	60	16	3600	240		Sxy	114		xc (volume as axis,mL) (ppm)	12.10526316
7	SUM	10	183	30	7999	480					xc (conc. as axis, ppm) (ppm)	6.052631579
8	(SUM xi)^2	100						m	11.4			
9	(SUM yi)^2	33489						b	13.8		Note: LINEST can calculate some of these numbers for you	
10											Linest Output	
11								sr	0.73029674		m	b
12								sm	0.23094011		sm	sb
13								sb	0.56568542		r^2	sr
14								sc	0.07106881		F	N-2
15												
16								t (N-2)	3.182			
17											Linest Output	
18								95%CI			11.4	13.8
19								slope (m)	0.73495449		0.230940108	0.565685425
20								Intercept (b)	1.80026349		0.998770366	0.730296743
21								x-intercept	0.22617268		2436.75	3
22											1299.6	1.6
23												
24											matches what we calculated!	
25												

We will create a spreadsheet to make these standard addition calculations!