

# Method of Standard Additions (MSA/SA)



# Definition

The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution, compensating for a sample constituent that enhances or depresses the analyte signal.

For multi-point, the absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis.

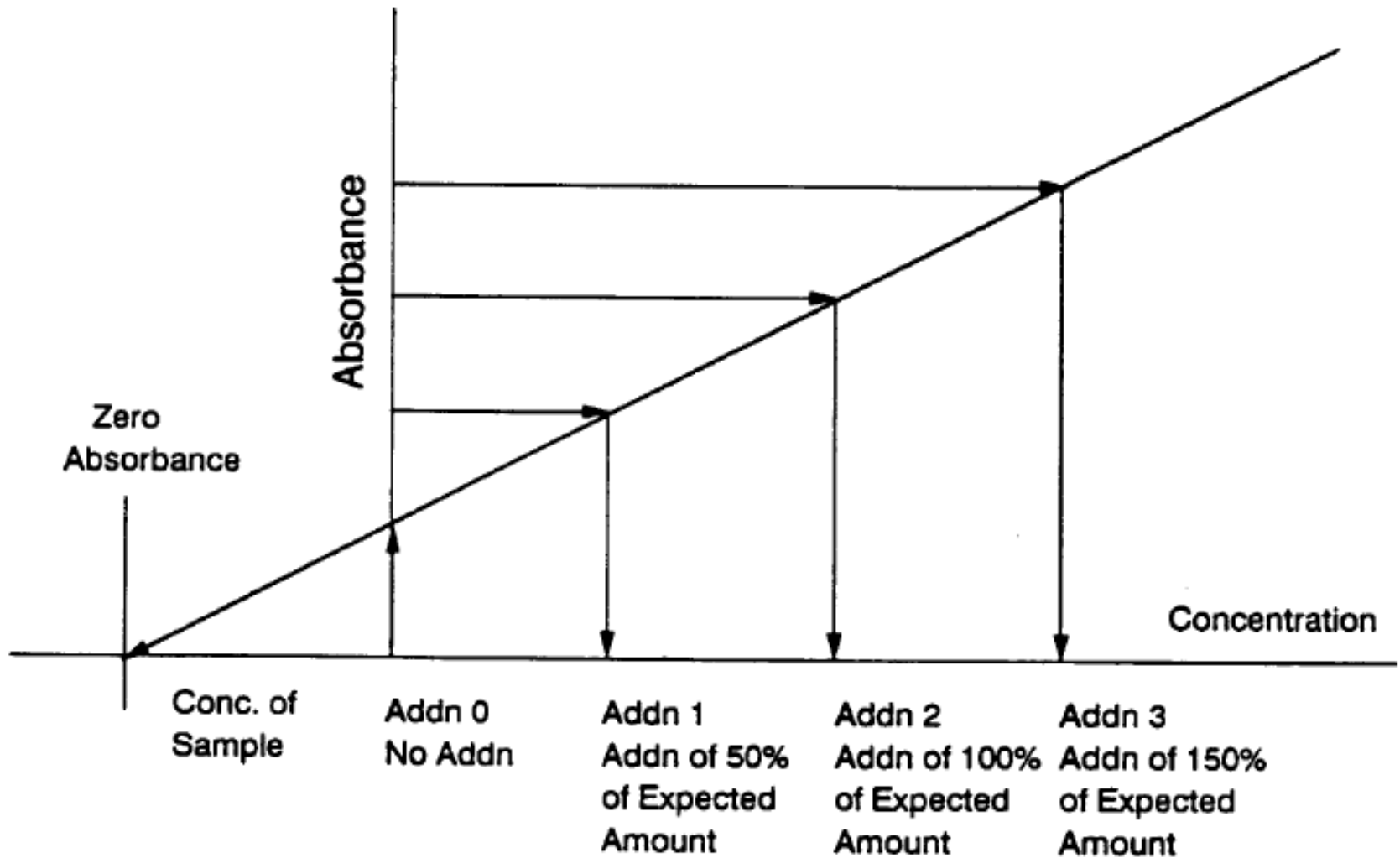


## Definition Cont.

When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

*SW-846 7000B/7010 Section 9.7*





**A linear regression program may be used to obtain the intercept concentration:**

$$Y = mx + b$$

**Where m = slope**

**b = y intercept**

**TRUE VALUE OF SAMPLE:                    2 x(-b)**



A

B

C

METHOD OF

STANDARD

ADDITIONS

True Value of standard is half because std is diluted 1:1 with sample

**SAMPLE ID:**  
**20060080635 DATE:**  
**08/09/06**

Instrument reading/output (x)

Concentration of Standard (y)

162741

0

0

337355

2.5

5

479670

5

10

776965

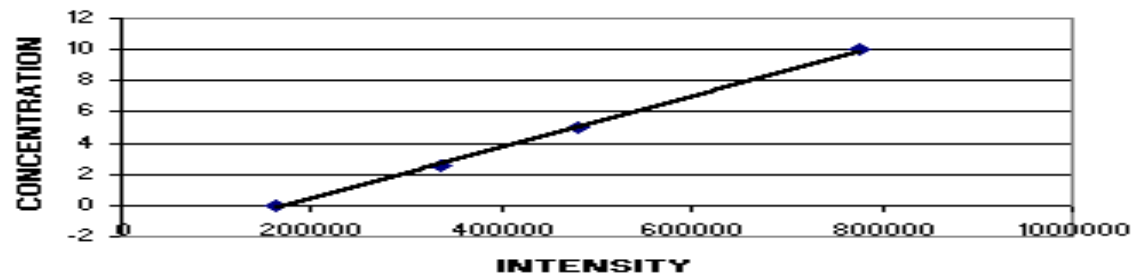
10

20

### METHOD OF STANDARD ADDITIONS

$$y = 0.0000164211x - 2.8368771627$$

$$R^2 = 0.9986117222$$



Find slope and y intercept

The equation of a line may be expressed as:

$$y = mx + b$$

where:

m = slope

b = y intercept

TRUE VALUE OF SAMPLE:

$$2 \times (-b)$$

(dilution factor of 2)

5.673754325

m:

0.0000164211

b:

-2.836877163

The r2 must be at least

.995

The slope must be within 20% of original calibration slope

True Value of Sample is equal to the Absolute Value of y-intercept

First slope (CALIBRATION)

0.0000152500

Second slope (MSA)

0.0000164211

Rel % deviation

7.395385699

(Must be  $\leq$  20%)

# Limitations of MSA

1. Must be linear over the conc. range of concern. The slope of the MSA plot should be < than 20% difference from the original standard curve.
2. Effect of the interference should not vary as the ratio of analyte conc. to sample matrix changes, and the SA should respond in a similar manner as the analyte.
3. Must be free of spectral interference and corrected for nonspecific background interference.



***Ref: SW-846 7000B, Section 8.7 & 7010, Section 9.7***

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# Benefit

When matrix effects appear or are to be expected and matrix-matched calibration samples are not available, the standard addition method (SAM) can be the calibration method of choice.

*IUPAC 1998, Pure and Applied Chemistry 70, 993-1014*



# Disadvantages

1. Time consuming to perform a full calibration for one sample.
2. It will not correct for additive interferences which cause a baseline shift.
3. Inaccuracies in preparing the spiked samples can seriously affect the slope of the line, causing errors to be made in the determining the original concentration.

*Ref: Kelley, William D.; Ratliff, Jr., Thomas A.; and Nenadic, Charles. (1992). Basic Statistics For Laboratories: A Primer for Laboratory Workers.*



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