

Chapter 5 - Quality Assurance and Calibration Methods

- I. Quality Assurance
- II. Figures of Merit
- III. Standard Additions
- IV. Internal Standards

I. Quality Assurance

“What we do to get the right answer for our purpose” (pg 78)

Data quality standards:

- Get the right data
- Get the data right
- Keep the data right

Table 5-1 Quality assurance process

Question	Actions
Use Objectives Why do you want the data and results and how will you use the results?	<ul style="list-style-type: none">• Write use objectives
Specifications How good do the numbers have to be?	<ul style="list-style-type: none">• Write specifications• Pick methods to meet specifications• Consider sampling, precision, accuracy, selectivity, sensitivity, detection limit, robustness, rate of false results• Employ blanks, fortification, calibration checks, quality control samples, and control charts to monitor performance• Write and follow standard operating procedures
Assessment Were the specifications achieved?	<ul style="list-style-type: none">• Compare data and results with specifications• Document procedures and keep records suitable to meet use objectives• Verify that use objectives were met

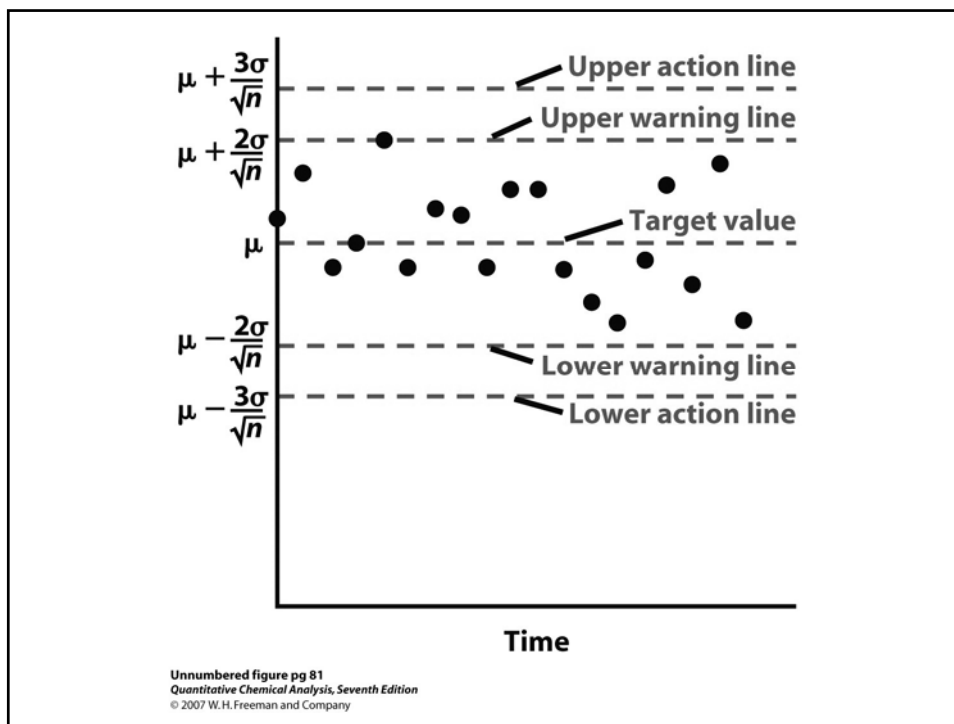
Table 5-1
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I. Quality Assurance (cont.)

One tool to use: *Control Charts*

- Visual representation of a confidence interval
- Can be used to monitor a process, product, or instrument

First, how would the Gaussian curve change if each point were not based on one measurement, but the average of n measurements?



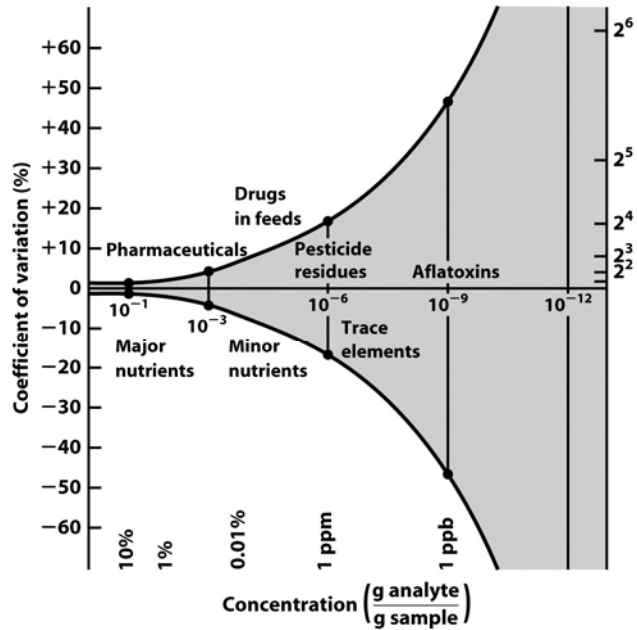
II. Analytical Figures of Merit

What are some quantitative ways of comparing analytical instruments and methods?

1. Sensitivity
2. Limit of Detection
3. Lower Limit of Quantitation
4. Linear Range
5. Linearity
6. Accuracy
7. Precision

Horwitz
Trumpet:

Based on
review of 150
interlab
studies



Unnumbered figure pg 85
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III. Standard Additions

Definitions:

1. matrix – everything in the analytical sample, except the analyte
2. matrix effect – change in analytical signal caused by the matrix

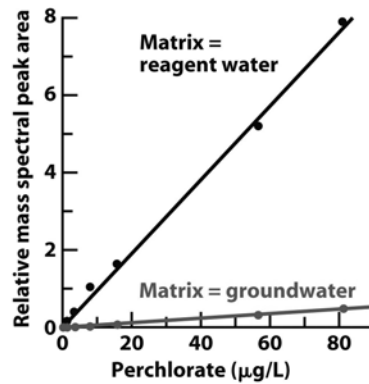


Figure 5-3
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III. Standard Additions (cont.)

Method of Standard Additions –

- used to overcome matrix effects
- known amounts of standard are added directly to the analytical sample
- matrix affects both the original and added analyte

III. Standard Additions (cont.)

A. One-point standard addition

Ex: Exercise 5-B (pg 92)

An unknown sample of Ni^{2+} gave a current of $2.36 \mu\text{A}$ in an electrochemical analysis. When 0.500 mL of solution containing 0.0287 M Ni^{2+} was added to 25.0 mL of unknown, the current increased to $3.79 \mu\text{A}$. Find the concentration of Ni^{2+} in the unknown.

III. Standard Additions (cont.)

B. Multi-point standard addition

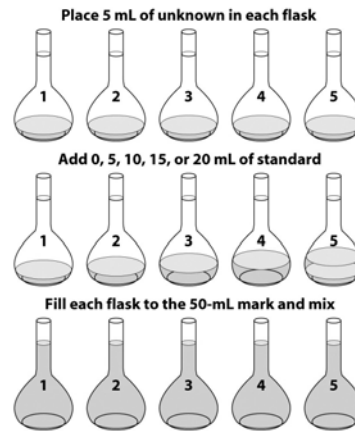
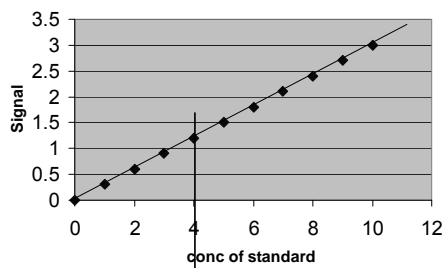
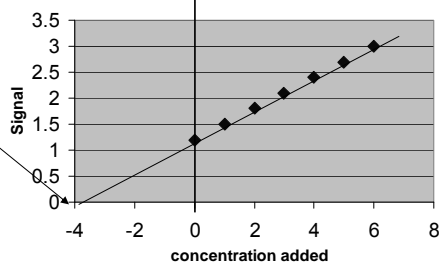


Figure S-4
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Calibration Plot



Standard Additions Plot

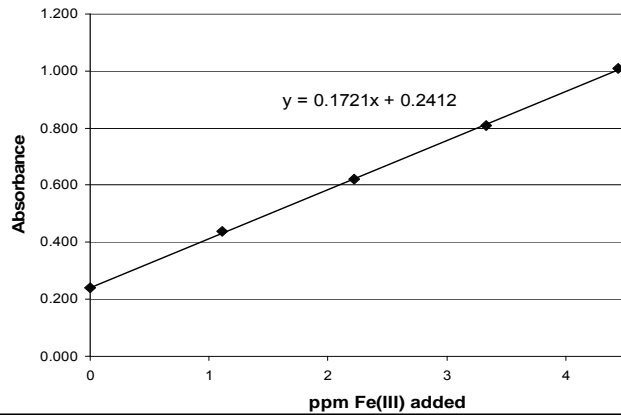


initial concentration =
 $-[\text{analyte}]$

Method of Standard Additions

Example:

Five 10-mL aliquots of a natural water sample were pipetted into separate 50.00-mL volumetric flasks. Exactly 0.00, 5.00, 10.00, 15.00, and 20.00 mL of a standard solution containing 11.1 ppm of Fe^{3+} were added to each, followed by an excess of thiocyanate to give the red complex $\text{Fe}(\text{SCN})^{2+}$. After dilution to volume, absorbances for the five solutions were found to be 0.240, 0.437, 0.621, 0.809, and 1.009 respectively. What was the concentration of Fe^{3+} in the water sample?



IV. Internal Standards

Another big problem for the analytical chemist –

Instrument response may vary from run to run for the same concentration of analyte

Why does this happen?

- injection volume may be hard to reproduce (Gas Chromatography)
- some analyte may be lost during preparation of the sample
- instrument detector sensitivity may change

IV. Internal Standards (cont.)

Solution:

Internal Standard -

compound, different from the analyte, added to all samples, blanks, and calibration standards in a known amount

Equation Derivation:

$$\frac{(\text{signal ratio})_{\text{unknown}}}{(\text{signal ratio})_{\text{known}}} = \frac{(\text{concentration ratio})_{\text{unknown}}}{(\text{concentration ratio})_{\text{known}}}$$

$$\frac{S_{\text{analyte, unknown}} / S_{\text{IS, unknown}}}{S_{\text{analyte, known}} / S_{\text{IS, known}}} = \frac{[\text{analyte}]_{\text{unknown}} / [\text{IS}]_{\text{unknown}}}{[\text{analyte}]_{\text{known}} / [\text{IS}]_{\text{known}}}$$

$$\frac{S_{\text{analyte, unknown}}}{[\text{analyte}]_{\text{unknown}}} = \frac{\boxed{\frac{S_{\text{analyte, known}}}{S_{\text{IS, known}}} \frac{[\text{analyte}]_{\text{known}}}{[\text{IS}]_{\text{known}}}} \frac{S_{\text{IS, unknown}}}{[\text{IS}]_{\text{unknown}}} = F$$

$$\frac{S_{\text{analyte, unknown}}}{[\text{analyte}]_{\text{unknown}}} = F \frac{S_{\text{IS, unknown}}}{[\text{IS}]_{\text{unknown}}} \quad \text{Equation 5-11}$$

IV. Internal Standards (cont.)

Ex: Exercise 5-C (pg 92)

A solution was prepared by mixing 5.00 mL of unknown (element X) with 2.00 mL of solution containing 4.13 μg of standard (element S) per milliliter, and diluting to 10.0 mL. The measured signal ratio in an atomic absorption experiment was $(\text{signal due to X}) / (\text{signal due to S}) = 0.808$. In a separate experiment, for equal concentrations of X and S, the signal due to X was found to be 1.31 times more intense than the signal due to S. Find the concentration of X in the unknown.