

Quality Assurance

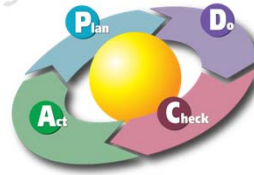
Two Key Questions:

1. What are the goals/outcomes of analytical process?
2. Do the products of the process (results) meet the objectives?
How do we know?

Applicable in a variety of settings: Lab, Manufacturing, Business...

Lots of Philosophies:

Total Quality Management
Six Sigma (99.99966%)
PDCA



Use Objectives: For what will the results be used?

Specifications: How good do the numbers need to be? How do we check to be sure they are that good?

1

General Approach to Quality Assurance

TABLE 5-1 Quality assurance process

Question	Actions
<i>Use Objectives</i> Why do you want the data and results and how will you use the results?	<ul style="list-style-type: none"> • Write use objectives
<i>Specifications</i> 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
<i>Assessment</i> 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

Harris, *Quantitative Chemical Analysis*, 8e
© 2011 W. H. Freeman

2

Quality Descriptors and Figures of Merit

Assessing Accuracy

- Calibration checks with known samples
- Fortification recoveries
- Quality control samples (blind samples)
- Blanks

Blanks :

- Reagent blank
- Method blank

Spiked (fortified) Samples

- % Recovery

3

Quality Descriptors and Figures of Merit

Assessing Precision

- Replicate samples
- Replicate portions of the same sample

Sensitivity vs Selectivity

Influence of concomitants and **matrix** effects

- How do we deal with this?

Linearity

- Closeness of fit

Range

- Concentration range over which specifications are met
- LDR

Robustness

4

Quality Descriptors and Figures of Merit

Limits of Detection (LOD) and Quantitation (LOQ)

Amount of analyte that is “significantly different” from the blank.

- Need:
 1. A measure of the precision of the method
 2. The relationship between analyte concentration and response of method

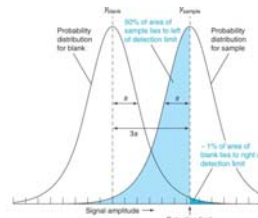
To determine LOD/LOQ

1. Determine the minimum detectable signal (y_{dl})

$$y_{LOD} = y_{blank} + 3s \quad y_{LOQ} = y_{blank} + 10s$$

2. Convert y_{dl} to an **amount of analyte** (i.e. concentration)

$$y = m(\text{concentration}) + b$$



5

Quality Assessment

How do we

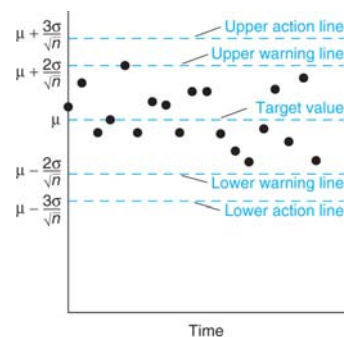
1. Show that our procedure is operating within specifications?
2. Verify that results meet use objectives?

DOCUMENTATION!!

Standard Operating Procedures (SOPs)

Recordkeeping and Process Monitoring

QC Samples
Control Charts



Harris, *Quantitative Chemical Analysis*, 8e
© 2011 W. H. Freeman

6

Dealing with Challenging Circumstances: Matrix Effects

Real sample matrices can be complex

- Hard to prepare reasonable blanks
- Matrix may influence response of the analyte

Method of Standard Additions

1. Add a known amount of standard to the sample solution itself.
Standard has the same identity as the analyte
2. Perform the analysis.
3. The resulting signal is the sum of the signal for the sample and the standard.
4. By varying the concentration of the standard in the solution, it is possible to extract a value for the response of the unknown itself.

$$\frac{[X]_i}{[S]_f + [X]_f} = \frac{I_X}{I_{S+X}}$$

How does this work in practice?

7

Standard Additions In Practice

Graphically relate response to the concentration of standard added

One common approach:

1. Prepare a series of solutions with the same unknown analyte concentration and varying, but known, added standard concentrations.
2. Analyze each solution
3. Plot response as a function of concentration of standard added
4. Determine least-squares line
5. Concentration of the unknown (as measured) corresponds to the x-intercept of the plot

$$S_{x-int} = \frac{S_y}{m} \sqrt{\frac{1}{n} + \frac{\bar{y}^2}{m^2 \sum (x_i - \bar{x})^2}}$$

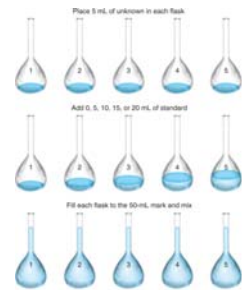
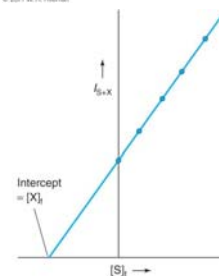


FIGURE 5-7 Standard addition experiment with constant total volume.
Harris, Quantitative Chemical Analysis, 8e
© 2011 W. H. Freeman

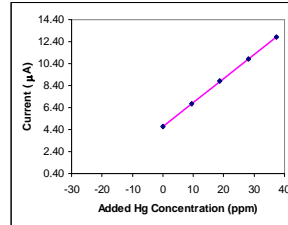


8

Standard Additions Example

Hg added (ppm)	Current (μA)
0	4.66
9.36	6.76
18.72	8.83
28.08	10.86
37.44	12.8

$$y = (0.217735 \mu\text{A/ppm})x + 4.706 \mu\text{A}$$



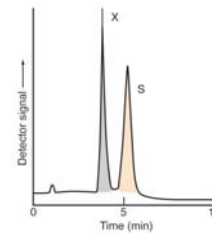
9

Dealing with Challenging Circumstances: Run to Run Variation

Some measurements have inherent variability that makes calibration curves and standard additions difficult to execute. In those cases, an **internal standard** is used to complete the determination.

To run an analysis using an internal standard:

1. Prepare a solution containing the unknown and a known concentration of the internal standard
Internal Standard has a *different identity* than the unknown
2. Perform the analysis on this mixture
3. The concentration of the unknown can be determined
AS LONG AS the *response factor* is known.



Response factor: constant relating the response of a fixed concentration of component A to the same concentration of component B.

$$\frac{\text{Analyte Signal}}{\text{Analyte Concentration}} = F \left(\frac{\text{Standard Signal}}{\text{Standard Concentration}} \right)$$

NOTE: The concentrations are the concentrations of the species *in the mixture that was analyzed*.

10

Internal Standards In Practice

