

Statistics

1. What is the relation between the standard deviation and the precision of a procedure? What is the relation between standard deviation and accuracy?

Solution:

Smaller standard deviation means better precision, no necessary relationship between standard deviation and accuracy

2. What is the meaning of a confidence interval?

Solution:

Confidence interval is region around around measured mean in which true mean is likely to lie; 95% of confidence intervals generated using a given method at the 95% confidence level will contain the true value of the parameter being measured

3. List the three different cases studied for comparison of means, and write the equation used in each case.

Solution:

Case 1: Compare measured result to known value, using

$$\bar{x} \pm \frac{ts}{\sqrt{n}}$$

To generate a confidence interval

Case 2: Compare replicate measurements, using

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

if the standard deviations are the same, or

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{s_1^2/n_1 + s_2^2/n_2}}$$

if the standard deviations are significantly different

Case 3: Compare individual differences, using

$$s_d = \sqrt{\frac{\sum (d_i - \bar{d})^2}{n - 1}}$$

and

$$t_{\text{calculated}} = \frac{|\bar{d}|}{s_d} \sqrt{n}$$

if different methods are used to make single measurements on several samaples without replication

4. How can you determine whether or not two standard deviations are statistically different?

Solution:

Use the F test, $F = s_1^2/s_2^2$

5. The percentage of an additive in gasoline was measured six times with the following results: 0.13, 0.12, 0.16, 0.17, 0.20, 0.11%. Find the 90% and 99% confidence intervals for the percentage of the additive.

Solution:

90%: 0.148 ± 0.028 ; 99%: 0.148 ± 0.056

6. A trainee in a medical lab will be released to work on her own when her results agree with those of an experienced worker at the 95% confidence level. Results for a blood urea nitrogen analysis are shown below:

Trainee: $\bar{x} = 14.57$ mg/dL, $s = 0.53$ mg/dL, $n = 6$ samples

Experienced worker: $\bar{x} = 13.95$ mg/dL, $s = 0.42$ mg/dL, $n = 5$ samples

- (a) What does the abbreviation dL stand for?
(b) Should the trainee be released to work alone?

Solution:

- (a) deciliter = 0.1 L
(b) yes ($t_{\text{calculated}} = 2.12 < t_{\text{table}} = 2.262$)

Spectroscopy

7. The molar absorptivities of compounds X and Y were measured with pure samples of each:

λ (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	
	X	Y
272	16400	3870
327	3990	6420

A mixture of compounds X and Y in a 1.000-cm cell had an absorbance of 0.957 at 272 nm and 0.559 at 327 nm. Find the concentrations of X and Y in the mixture.

Solution:

$[\text{X}] = 4.43 \times 10^{-5} \text{ M}$
 $[\text{Y}] = 5.95 \times 10^{-5} \text{ M}$

Quality Assurance and Calibration

8. What is the difference between a calibration check and a performance test sample?

Solution:

Calibration check sample is made by the analyst to check the calibration of the instrument; performance test sample is made by someone else to check the performance of the analyst

9. How is a control chart used? State six indications that a process is going out of control.

Solution:

A control chart warns when a property being monitored strays dangerously far from an intended target value.

Indications that a process is going out of control include:

- one observation outside the action lines
- two out of three consecutive measurements between the warning and action lines
- seven consecutive measurements all above or all below the center line
- six consecutive measurements all steadily increasing or all steadily decreasing, wherever they are located
- 14 consecutive points alternating up and down regardless of where they are located
- an obvious nonrandom pattern

10. Low concentrations of EDTA near the detection limit gave the following dimensionless instrument readings: 175, 104, 164, 193, 131, 189, 155, 133, 151, and 176. Ten blanks had a mean reading of 45.0. The slope of the calibration curve is $1.75 \times 10^9 \text{ M}^{-1}$. Estimate the signal and concentration detection limits and the lower limit of quantitation for EDTA.

Solution:

Signal detection limit:

$$y_{\text{dl}} = y_{\text{blank}} + 3s = 129.6$$

Detection limit:

$$\text{Minimum detectable concentration} \equiv \frac{3s}{m} = 4.8 \times 10^{-8} \text{ M}$$

Quantitation limit:

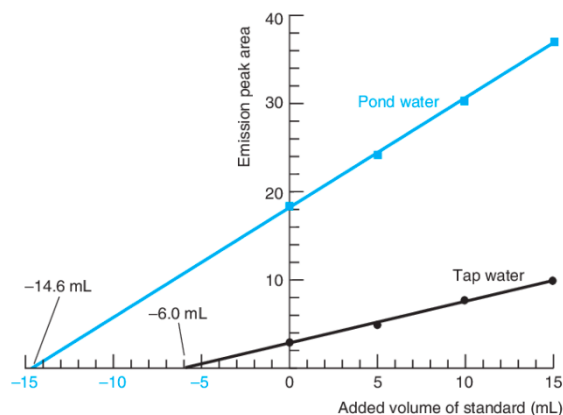
$$\text{Lower limit of quantitation} \equiv \frac{10s}{m} = 1.6 \times 10^{-7} \text{ M}$$

11. Why is it desirable in the method of standard additions to add a small volume of concentrated standard rather than a large volume of dilute standard?

Solution:

Addition of a small volume keeps the matrix nearly constant by not diluting the sample.

12. Europium is a lanthanide element found at parts per billion levels in natural waters. It can be measured from the intensity of orange light emitted when a solution is illuminated with ultraviolet radiation. Certain organic compounds that bind Eu(III) are required to enhance the emission. The figure below shows standard addition experiments in which 10.00 mL of sample and 20.00 mL containing a large excess of organic additive were placed in 50-mL volumetric flasks. Then Eu(III) standards (0, 5.00, 10.00, or 15.00 mL) were added and the flasks were diluted to 50.0 mL with water. Standards added to tap water contained 0.152 ng/mL of Eu(III), but those added to pond water were 100 times more concentrated (15.2 ng/mL).



- (a) Calculate the concentration of Eu(III) (ng/mL) in pond water and tap water.

Solution:

Tap water: 0.091 ng/mL; pond water: 22.2 ng/mL