Basic statistical tools for analytical laboratories

Chapter 6
Significance (Hypothesis) Testing

Significance (Hypothesis) Testing

- Very often, our scientific problem is not so much the estimation of a population parameter but is to make decisions and conclusions on the data we have collected.
- A statistical hypothesis is a statement or assumption concerning one or more populations.
- A test statistic is a statistical procedure that leads us to the truth or falsity of a hypothesis made.

Significance (Hypothesis) Testing

- A test statistic is the basic form of **ANOVA** (Analysis of Variance)
- To test if there is any significance difference between:
- **Two standard deviations**
- **Two means or experimental data**
- **Test result against the 'true' value**
- Important for checking result bias and significance of spiked recoveries, because all measurements should be free from systematic error.

Significance (Hypothesis) Testing

- A Null hypothesis H_o refers to any hypothesis that we want to test : the rejection of H_o leads to the acceptance of an alternative hypothesis, denoted by H_1
- A null hypothesis → an exact value of a parameter, and an alternative hypothesis allows for the possibility of other values.
- Always begin by assuming H_o is true until proven otherwise by the test statistic.

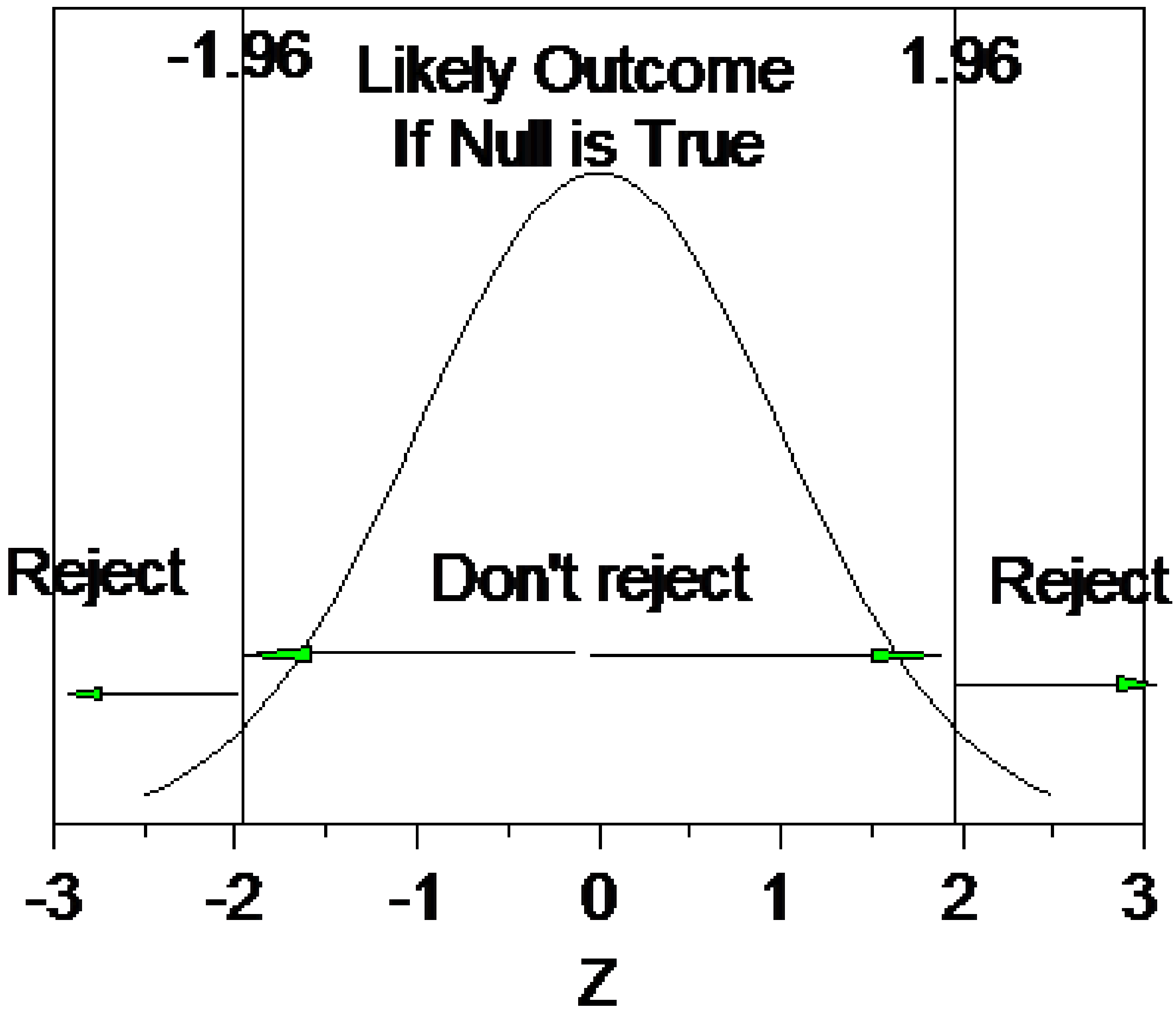
Significance (Hypothesis) Testing

- Example:
- H_o : $\mu = 30$ mg/L
- H_1 : $\mu \neq 30$ mg/L

- Draw one of the **2 conclusions** after a test statistic:
- 1) Reject H_o and accept H_1
- 2) Accept H_o is true

Significance (Hypothesis) Testing

- **Steps of significance testing**:
- **Null H_o** : no significant difference between 2 values, $a = b$ at α =0.95 (or 95%) probability level (i.e. on average, a 1 in 20 chance to reject the null hypothesis *when it is in fact true)*
- **Alternate H_1** : there is a difference, or lesser or larger between them, $a > b$, $a < b$ or $a \neq b$
- Carry out a test statistic, e.g. ***F*** – test or ***t*** – test


-1.96
Likely Outcome
If Null is True
1.96
Reject
Don't reject
Reject
-3
-2
-1
0
1
2
3
Z

Significance (Hypothesis) Testing

- **Steps of significance testing (contd):**
- Evaluate the test statistic result against the given critical value of the test from the relevant table
- Make a decision and conclusion
- Note: $a \neq b$: two–sided test table
- $a > b$: one–sided test table
- $a < b$: one–sided test table

F-Test

- To test for any significant difference between random errors as variances (s^2 or σ^2) in ***a*** population
- $F = s_1^2 / s_2^2 > 1$
- *with degrees of freedom* v_1 *and* v_2
- Compare the F result against the critical values in the F-Table
- F test can also be applied on two populations with two variances:

$$F = \frac{s_a^2 / \sigma_a^2}{s_b^2 / \sigma_b^2}$$

F-Test : Example

Trial #	Analyst A, ppm	Analyst B, ppm
1	14.5	15.6
2	13.2	14.1
3	13.8	15.9
4	13.9	14.8
5	14.8	16.2
Mean =	14.0	15.4
Std Dev =	0.627	0.858
Variance =	0.393	0.737
F-value =	1.875	
F(4,4) Critical 2-tail	9.605	
F(4,4) Critical 1-tail	6.388	

Ho : Var(A) = Var (B)

H1: Var(A) ≠ Var (B) (2-Tail)

Var(A) < Var (B) (1-Tail)

Verdict : NO significant differences between Var(A) and Var(B).

Student's t-Tests

- 1) Test against a reference or assigned value:

$$\mu = x \pm t\,(s / \sqrt{n})$$

- or,

$$t = | \mu - x | \sqrt{n} / s$$

- *Example….*

t-Test against reference value

Certified ref value μ = 250.0 mg/L

Replicated analysis :

Trial #	x, mg/L
1	239
2	256
3	265
4	246
5	242
6	236
Mean =	247.3
Std Dev =	11.094
n =	6
t-Value =	0.589
Critical t(5)=	2.571

$t = | \mu - x | \sqrt{n} / s$

As *t*-value < *t* (critical), the mean value is not significantly different from the certified value.

Student's t-Tests

- 2) To compare two mean results of 2 analysts, or labs, or methods
- $$t = \frac{(\bar{x}_1 - \bar{x}_2)}{S_p\sqrt{(1/n_1 + 1/n_2)}}$$
- where
  $S_p = \sqrt{\{[\, s_1^2(n_1 - 1) + s_2^2(n_2 - 1)] / (n_1 + n_2 - 2)\}}$
- *Example ….*

t-Test for two means

Trial #	Analyst A, ppm	Analyst B, ppm
1	14.5	15.6
2	13.2	14.1
3	13.8	15.9
4	13.9	14.8
5	14.8	16.2
Mean =	14.04	15.32
Std Dev =	0.627	0.858
Variance =	0.393	0.737
Sp^2 =	0.565	
t-value =	2.693	
t(8) Critical =	2.306	

Verdict: The mean value of Analyst A is significantly different from that of Analyst B.