Treatment of Analytical Data

I. Accuracy vs. Precision
   A. Accuracy

   B. Precision

   C. Use of Precision to Infer Accuracy

II. Precision

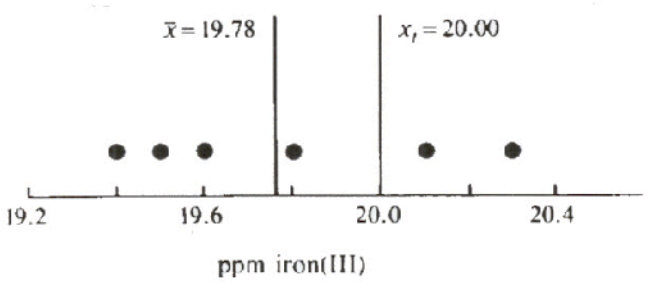
   A. Range

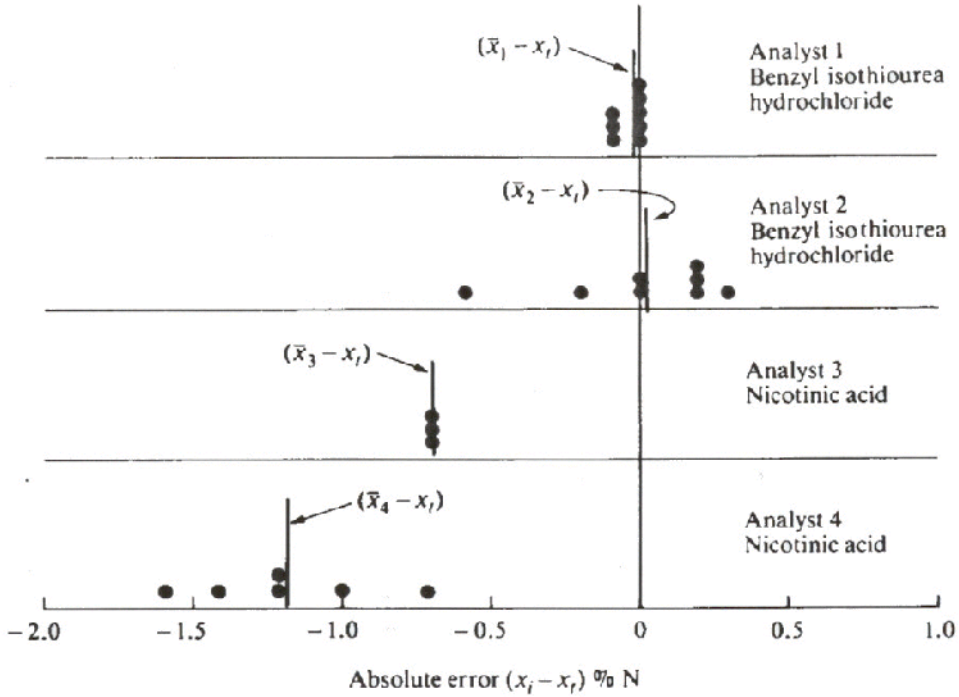
   B. Average Deviation

   C. Standard Deviation

   D. Standard Error of the Mean

E. Confidence Limits


$\bar{x} = 19.78$
$x_t = 20.00$
19.2
19.6
20.0
20.4
ppm iron(II)


$(\bar{x}_1 - x_t)$
Analyst 1
Benzyl isothiourea hydrochloride
$(\bar{x}_2 - x_t)$
Analyst 2
Benzyl isothiourea hydrochloride
$(\bar{x}_3 - x_t)$
Analyst 3
Nicotinic acid
$(\bar{x}_4 - x_t)$
Analyst 4
Nicotinic acid
−2.0
−1.5
−1.0
−0.5
0
0.5
1.0
Absolute error $(x_i - x_t)$ % N

III. Error - Measure of Accuracy

A. Let

X = Ave of Triplicate Determinations

μ = True Value

B. Absolute Error = X - μ

C. Relative Error = $\frac{|X - \mu|}{\mu} \times 100 \ (\% \ Error)$

1. Expressed as

pph $\frac{X - \mu}{\mu} \times 100 =$ ------ pph

% error ------ %

ppt = $\frac{X - \mu}{\mu} \times 1000 =$ ------ ppt

2. Eg

pph =

ppt =

IV. Types of Error

A. Determinate Error (Systematic Error)

B. Two Types of Determinate Error

1. Constant Error (Additive Error)

a. Magnitude of error is constant regardless of sample size.
Absolute error is constant.

b. Relative error ↓ as sample size ↑

2. Proportional Error

a. Absolute error ↑ with ↑ sample size
Relative Error remains constant

b. Interfering substances in sample

C. Indeterminate Error - Random Error

1. Random fluctuations occur when one pushes a method to its limits of accuracy

2. Data with Random Error vs. Less Precise Data with No Random Error

V. Methods of Expressing Uncertainty in Results

A. Three methods

1. Record Uncertainty (Absolute)

2. Record Relative Uncertainty in %

3. Use of Significant Digits

a. Record all accurately known digits + a digit that is uncertain

b. Method assumes that the last digit recorded is uncertain by 1 unless stated differently

B. Rules for Significant Digits

1. Digits 1 → 9

2. Zeros between Significant Digits

3. Terminal Zeros to Right of Decimal

4. Terminal Zeros to Left of Decimal
(two thoughts)

5. Place holding zeros

Except log x = 0.025

C. Mathematical Manipulation of Numbers and Significant Figures

1. Addition & Subtraction
   (rules of rounding numbers off)

2. Multiplication and Division of Measurements

3. Multiplication and Division of a Measurement by a Constant

4. Logs - Same number of significant figures to the right of the decimal as the total number of significant figures in the non-exponential number used to calculate the log

   a. $[H^+] = 6.6 \times 10^{-11}$

      ↑ ↑ Exponential

      non exponential

   b. $pH = -\log [H^+] = - \log (6.6 \times 10^{-11})$

D. Use of Absolute and Relative Uncertainties in Mathematical Manipulations

1. Addition and Subtraction

   a. Rule: Add Absolute Uncertainties

   b. Final Buret 48.26 ml ± .02 ml

      Initial Buret Reading 0.15 ml ± .02 ml

      Volume Delivered =

2. Multiplication & Division

   a. Rule: Calculate % uncertainty for each number and add the % uncertainties

   b. $\frac{325.0 \text{ ml} \pm .02\% \times 5.200 \text{ N} \pm 0.1\%}{3.100 \text{ N} \pm 0.1\%}$

E. Use of Standard Deviations in Mathematical Manipulations - Propagation of Uncertainties

1. Reminder that standard deviation of <20

$$s = \sqrt{\frac{\sum |\bar{x} - x_i|^2)}{(N-1)}}$$

2. Addition and Subtraction

$$\begin{array}{ll} & a\ (\pm s_a) \\ + & b\ (\pm s_b) \\ - & c\ (\pm s_c) \\ \hline y = & \pm s_y \end{array}$$

$$s_y = \sqrt{s_a^2 + s_b^2 + s_c^2} = \sqrt{\sum Variances}$$

Example - Perform the following operations and compute an uncertainty for the resulting number

$$
\begin{array}{ll}
 & 0.50\ (\pm\ 0.02) \\
+ & 4.10\ (\pm\ 0.03) \\
- & 1.97\ (\pm\ 0.05) \\
\hline
 & 2.63 \pm\ ?
\end{array}
$$

3. Multiplication and Division

$$y = \frac{a\ (\pm s_a) \times b\ (\pm s_b)}{c\ (\pm s_c)}$$

Relative Standard Deviations

$$\frac{s_a}{a} \qquad \frac{s_b}{b} \qquad \frac{s_c}{c}$$

$$s_y/y = \sqrt{(s_a/a)^2 + (s_b/b)^2 + (s_c/c)^2}$$

Example -

$$\frac{4.10\ (\pm 0.02) \times 0.0050\ (\pm 0.0001)}{1.97\ (\pm\ 0.04)}$$

VI. Rejection of Data

A. Things You May Do

1.

2.

3.

B. Statistical Rejection Tests

1. 2.5 d Rule

a. Approach

b. Problem

2. 4 d Rule

a. Approach

b. Problem

3. Q Test

a. Approach

$$Q = \frac{\text{gap}}{\text{range}}$$

b. Values of Q

# Observations	$Q_{0.90}$	# Observations	$Q_{0.90}$
3	0.94	6	0.56
4	0.76	7	0.51
5	0.64	8	0.47

c. Example

.10525
.10651
.10663

Q = _____

d. What Can We do if a Result Must Be Retained?

1. Estimate Precision

2. Check Calculations

3. Repeat Analysis

4. Try Q Test With Additional Data Point