5 Errors in Chemical Analyses: Assessing the Quality of Results

5A Some Important Terms

Replicates:

the same size samples are carried through an analysis in exactly the same way (2~5).

5A-1 The Mean and Median

Mean, arithmetic mean, and average (\( \bar{x} \)):

\[
\bar{x} = \frac{\sum \limits_{i=1}^{N} X_i}{N}
\]

Median: the middle value in a set of data

Ex 5-1. Calculate the mean and median for the data: 19.4, 19.5, 19.6, 19.8, 20.1 and 20.3

\[
\text{Mean} = \bar{x} = \frac{19.4 + 19.5 + 19.6 + 19.8 + 20.1 + 20.3}{6} = 19.78 \approx 19.8 \text{ ppm Fe}
\]

\[
\text{Median} = \frac{19.6 + 19.8}{2} = 19.7 \text{ ppm Fe}
\]

5A-2 Precision

Precision: the closeness of results to others that have been obtained in the same way.

Deviation: \( d_i = |x_i - \bar{x}| \)

Standard deviation

Variance

Coefficient of variation
5A-3 Accuracy

Accuracy: the closeness of a measurement to the true or accepted value.

Absolute error: \( E = x_i - x_t \)

Relative error: \( E_r = \frac{x_i - x_t}{x_t} \times 100\% \)

Ex. Calculate the relative error of the data in ex.5-1 (true value = 20.00)

\[
E_r = \frac{19.8 - 20.00}{20.00} \times 100\% = -1\% \text{ or } -10 \text{ ppt}
\]

5A-4 Types of Errors in Experimental Data

Random, or indeterminate errors: affect the precision of measurement
Systematic, or determinate error: affect the accuracy of results
Gross errors: lead to outliers

Fig. 5-3 Absolute error in the micro-Kjeldahl determination of nitrogen. Each dot represents the error associated with a single determination. Each vertical line labeled \( (x_i - x_t) \) is the absolute average deviation of the set from the true value.
5B SYSTEMATIC ERRORS

5B-1 How do systematic errors arise?

   Instrument Errors
   Method Errors
   Personal Errors

5B-2 The effects of systematic errors on analytical results

   Constant errors: independent of the sample size
   Proportional errors: ↑ or ↓ ∝ sample size

<table>
<thead>
<tr>
<th>Ex. 5-2. Suppose that 0.50 mg of precipitate is lost as a result of being washed with 200 mL of wash liquid.</th>
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</thead>
<tbody>
<tr>
<td>If the ppt weights 500 mg, the relative error due to solubility loss is –(0.50/500) × 100% = –0.1%</td>
</tr>
<tr>
<td>If the ppt weights 50 mg, the relative error due to solubility loss is –(0.50/50) × 100% = –1.0 %</td>
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</tbody>
</table>

5B-3 Detection of systematic instrument and personal errors

5B-4 Detection of systematic method errors

   Analysis of standard samples
   Independent analysis
   Blank determinations
   Blank solution contains the solvent and all the reagents in an analysis but none of the sample.
   Variation in sample size