Analytical Chemistry

Analytical Chemistry

Analytical Chemistry: Identification and quantification of substance(s) (also termed as solutes, analytes, components) of interest in a material.

Qualitative analysis – What analyte(s) are present in a sample? or Is an analyte(s) of interest present?

Quantitative analysis – How much of the analyte(s) is there?

Analysis of molecular/chemical composition of materials of interest often (not always) necessitates the separation/isolation of an analyte(s) of interest from the sample (= mixture) before any type of further analysis (chromatography, extractions etc.).

An analyte is a substance or chemical constituent of a sample that is to be measured by an analytical method.

Methodology of chemical analysis:

* 1. Classical wet techniques; gravimetry and titrimetry.
   2. Instrumental methods; methods involving instrumentation; electrochemical-analysis, chromatography, spectroscopy. (may involve wet chemistry).

   classical wet techniques necessarily employs chemical reactions and the reaction stoichiometry as the basis of analysis, exclusively.

Stoichiometry is the relationship between the number of moles of the reactants and products of a balanced chemical reaction.

Whether analysis is routine (as in manufacturing industry) or otherwise, the main objective is to obtain information involving matter.
General Approach to Chemical Analysis

1. Selecting an analytical method (search literature for existing protocols or devise new methods)

2. Selecting a representative composite sample for analysis (Sampling).

3. Making a laboratory sample from the representative composite sample amenable for analysis protocol (homogeneous solution; masking of interfering species if necessary).

4. Analyzing the laboratory sample with the selected procedure in replicate, 3 – 6, 8 replicates. May use more than one analytical procedure (method) to confirm the result.

5. Perform the statistics on results. Report results, interpretation/conclusions

1. Analytical Method Selection (to analyze - laboratory sample):
   based on,
   accuracy and precision expected
   time constraints
   cost/number of analyses
   complexity of sample (possible interferences)

2. Sampling:
   Often the actual ‘subject’ under analysis is much larger than the laboratory sample.

   Truck load of coal (metal impurities)
   A Lake (for dissolved oxygen)
   Blood (lead)
   Stratosphere (ozone)

   Lot

   Sampling is the process of obtaining a representative composite sample (=bulk sample) from the lot.

   It is followed by the preparation of the laboratory sample.
Lot - normally heterogeneous; in the extreme - highly segregated

From the Lot ⇒ bulk sample = representative-composite of the lot

Bulk sample ⇒ laboratory sample – a homogeneous solution

3. **Laboratory sample:**

Random bulk sampling:
- **overall un-segregated** lot
- **Random homogeneous** lot

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>13</td>
<td>14</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>17</td>
<td>18</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>21</td>
<td>22</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>25</td>
<td>26</td>
<td>27</td>
<td>28</td>
</tr>
<tr>
<td>29</td>
<td>30</td>
<td>31</td>
<td>32</td>
</tr>
</tbody>
</table>

Divide the lot into small equal regions (matrix); use a ‘map’. Number (label) the regions. (Set up all numbers in a ‘lotto’ type random drawing). Draw a few numbers (regions) randomly.

Obtain equal amounts of material from the randomly picked regions; combine them; bulk sample.

Random bulk sampling:
- **inhomogeneous (segregated)** lot

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>13</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>16</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>19</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>22</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>25</td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>28</td>
<td>29</td>
<td>30</td>
</tr>
<tr>
<td>31</td>
<td>32</td>
<td>33</td>
</tr>
<tr>
<td>34</td>
<td>35</td>
<td>36</td>
</tr>
</tbody>
</table>

Divide bulk .... Pick numbers randomly.

Collect from the different areas proportionally:
- e.g. 1:2:7 number of samples from the three areas.

The laboratory sample for analysis is a homogeneous solution, most of the time.

Analyze equal aliquots of prepared lab sample in replicate.

(instrumental methods involve generating calibration curves/ internal standards/ standard addition techniques)

Workout the uncertainty/error (statistics) of the results.

Report results, interpretation/conclusions.

4. **Analysis**

Example: Chemical Analysis

Theobromine

![Theobromine](image)

Cafliene

![Cafliene](image)

Both, soluble in water.
Recent photograph from a Colorado Chocolate Factory.

Lot

Recent photograph from a Colorado Chocolate Factory.
The signal from the chromatograph by itself is not of value for quantitative analysis.

It is necessary to generate a calibration plot(s) for the analyte(s) of interest to quantify the analytes.

To generate a calibration plot, prepare a series of solutions of known concentrations of the analyte(s) (standards) and subject the standards to analysis under the same experimental conditions. Obtain the instrument responses for each analyte. (Details later).

A calibration plot relates the signal/response intensity to the concentration of the analyte (linear graph).

Sensitivity of an analyte for detection = slope of calibration plot.

Table 0-1 Analyses of dark and white chocolate

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Dark chocolate</th>
<th>White chocolate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theobromine</td>
<td>0.392 ± 0.002</td>
<td>0.010 ± 0.007</td>
</tr>
<tr>
<td>Caffeine</td>
<td>0.050 ± 0.003</td>
<td></td>
</tr>
</tbody>
</table>

Uncertainties are the standard deviation of three replicate injections of each extract.

Summary of results:

Sample standard deviation, s, is a measure of the reproducibility of the analysis (at a preliminary level).

Smaller s indicates a better analysis (better precision).

Relative standard deviation is a measure of the quality of the analysis; the smaller the better.

5. Data treatment:

Calibration plot

Instrument Response vs. c

Instrument Response = c

y = c

y = mc + b

Height or area of the peaks; y.

Different response factors (slope=sensitivity) of substances necessitates the generation of a calibration plot for each analyte.
Units:

Molar mass = **Formula mass**, g/mol

Formality = moles of substance per liter of solution, mol/L.  
* Molarity (M) - moles of a substance per liter of solution, **often used to mean formality**, mol/L.  
* Molality (m) - moles of substance per kg of solvent.  

Osmolarity - moles of particles per liter of solution, mol/L.  
* assumes the chemical form of the substance is unchanged? 

Percent Composition (parts per hundred):  

\[ \text{wt\%} = \frac{m_{\text{analyte}}}{m_{\text{sample}}} \times 10^2 \]  

\[ \text{vol\%} = \frac{\text{Vol of analyte}}{\text{Vol of sample}} \times 10^2 \]  

For aqueous solutions, often 1 ml is assumed to weigh 1g.  
therefore;  

\[ 1 \text{ ppm} = 1 \mu g / g = 1 \mu g / mL = 1 \mu g / L = 1 \mu g / mL = 1 \mu g / L \]  
\[ 1 \text{ ppb} = 1 ng / g = 1 ng / mL = 1 ng / L = 1 ng / mL = 1 ng / L \]  

*Parts per’ expressions can be used for volumes of analytes as well.  

\[ pX = -\log_{10} X \]  

Please revise the procedure for unit conversions.