An Introduction to Chemical Analysis

Analytical chemistry is the study of the chemical composition of materials.

Chemical analysis is the process used to determine the chemical composition.

Together they form perhaps the most important branch of chemical science. Chemical analysis is important in fields such as industrial processes, medicine, sport, crime, food safety etc. Chemical analysis enables predictions to be made about the properties of various materials.

Stainless steel behaves as it does not because of the iron content, but because of the presence of relatively low levels of several other elements: by knowing the levels of the other elements predictions can be made concerning the properties of the steel.

Polluted water does not have to look bad to be bad! Often, the invisibles are the worst: chemical analysis can tell us whether it is safe to swim in, or safe to drink. Biological analysis would also be necessary here.

Where is Chemical Analysis Used?

In the manufacturing sector, chemical analysis is needed throughout the production process:

- Obtaining and analysing samples of raw, intermediate and final products
- Monitoring wastes
- Product development
- Trouble-shooting production problems
- Maintenance of testing equipment

In the health area the health of patients under medical care depends on the analysis of

- A large range of biological samples
- Pharmaceuticals used for treatment

In the environmental monitoring area analysis includes:

- Heavy metals
- Toxic organic chemicals

What answers does it give?

Chemical analysis is an exact science. Be prepared to commit to an answer……. “the sample contains about” is not really an answer at all. Results may be qualitative or quantitative as shown in Figure 1.1

<table>
<thead>
<tr>
<th>QUALITATIVE ANALYSIS</th>
<th>QUANTITATIVE ANALYSIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Is species present in the sample?</td>
<td>How much of species is present</td>
</tr>
<tr>
<td>YES / NO</td>
<td>NUMBER VALUE</td>
</tr>
</tbody>
</table>

Fig 1.1 Classes of chemical analysis.
Class Exercise:
*Identify each of the following as being qualitative or quantitative:*

<table>
<thead>
<tr>
<th>Description</th>
<th>Qualitative or Quantitative</th>
</tr>
</thead>
<tbody>
<tr>
<td>The alcohol content of a blood sample with the result being sent through to the courts</td>
<td>Quantitative</td>
</tr>
<tr>
<td>Analysis to determine if a sample contained any contaminant</td>
<td>Qualitative</td>
</tr>
<tr>
<td>Analysis to determine how much contaminant is present in a sample</td>
<td>Quantitative</td>
</tr>
<tr>
<td>Analysis to determine the functional groups present in an organic species</td>
<td>Qualitative</td>
</tr>
</tbody>
</table>

For a result to be reliable the sample analysed **must** be representative of the bulk material. The sample analysed must maintain the percentage of the analyte and the matrix in the original material.

The **analyte** is the chemical species to be determined by the analysis, it may be an element or a compound. The **matrix** is the rest of the sample. In most cases the matrix forms the major part of the sample and may therefore interfere in the analysis of the analyte.

![Fig 1.2 The sample in chemical analysis](image)

Class Exercise:
*What methods are you familiar with for the sampling of:*

- **Solids**

- **Liquids**

- **Gases**
Complete or total analysis: is the determination of the entire chemical composition of a material.

Partial analysis: is the determination of one or two species within a material for example the manganese and chromium levels in steel.

Ultimate analysis: is the determination of the total amount of a species for example the acid content of piece an apple measures all the acids not just the malic acid content.

Matrix interference
As the matrix is the major constituent of a sample care must be taken to ensure that it does not interfere with the chemical analysis. To check a method is providing the expected answer standards are often analysed using the same method as is used on the sample. If the expected answer is not obtained and errors such as instrumental and operator are eliminated, then the problem may be matrix interference.

Table 1.1 Types of Matrix Interference

<table>
<thead>
<tr>
<th>Type</th>
<th>Moisture content</th>
<th>Other volatile species causing mass loss attributed to water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>Moisture content</td>
<td>Other species eg F reacting with the titrant, increasing titre and apparent hardness value</td>
</tr>
<tr>
<td>Matrix adds extra response in the analysis</td>
<td>Titration of water hardness (Ca and Mg)</td>
<td></td>
</tr>
<tr>
<td>Type 2</td>
<td>Colorimetry</td>
<td>Species reacting with analyte, preventing it from forming colour or changing its colour</td>
</tr>
<tr>
<td>Matrix changes response of analyte</td>
<td>Titration</td>
<td>Fluoride complexes Fe$^{2+}$ strongly it cannot be titrated with EDTA</td>
</tr>
</tbody>
</table>

Analytical methods rely on the basic premise that an equal response from sample and standard means the same concentration. If the standard does not have the matrix elements in the sample that are causing changes in the sample response, then it cannot account for them in the analysis.

Checking for matrix interference

Not all samples have an interfering matrix. Generally, the simpler the sample, the less likely that interferences are occurring. Table 1.2 compares some of the methods for checking if matrix interference is present.
Table 1.2 Methods of checking for matrix interference

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physically separate analyte from matrix and check for change in response (e.g. distillation, extraction)</td>
<td>Relatively simple</td>
<td>All physical separation steps introduce errors through losses in transfer</td>
</tr>
<tr>
<td>Add chemical reagent to mask (chemically remove) suspected interfering species and check for response</td>
<td>Simple and inexpensive</td>
<td>Is only effective if masking agent is available and interference is known</td>
</tr>
<tr>
<td>Add suspected matrix elements to standard and check for change in response</td>
<td>Simple and inexpensive</td>
<td>Matrix may not be known or minor unknown component is the culprit</td>
</tr>
<tr>
<td>Use different method of analysis which isn’t susceptible to interference</td>
<td>Simple and inexpensive</td>
<td>Another may not be available May have interferences of a different type and source</td>
</tr>
<tr>
<td>Use standard samples of known composition and similar matrix</td>
<td>Shows any errors clearly since correct answer is known</td>
<td>Standard samples can be difficult to obtain and are usually expensive</td>
</tr>
<tr>
<td>Add known amount of analyte to sample, check whether measured response increases by expected amount</td>
<td>Simple and inexpensive</td>
<td>Does not check for Type 1 interference</td>
</tr>
</tbody>
</table>
Table 1.3 Compensating for Matrix Interference

- Make standards with the same matrix as sample by:
  - adding appropriate amounts of matrix species to samples
  - use samples of similar matrix of known analyte composition as standards
- Physical separation
- Chemical masking
- Add known amounts of analyte to sample
- Use a different method

Dissolution of Samples
Most, but not all, chemical analyses require the sample to be in solution. When the sample is presented as a solid either the entire sample must be dissolved or just the analyte.

For organic samples this means that extreme care must be taken so as to not change the nature of the analyte. Processes of physical separation such as extraction or distillation must be used. These processes leave the matrix behind but as mentioned previously this can introduce further losses.

For inorganic analytes more drastic measures such as high temperature and strong acid treatments can be used. For insoluble materials such as rocks fluxing, heating vigorously with molten salts may be used. For organic matrixes, such as food, the sample may be ashed leaving behind the mineral matter which can then be dissolved.

Ashing
- Removes organic matter at temperatures up to 800°C (dry ashing) leaving the metallic elements in the form of oxides which can then be dissolved in nitric acid.
- Errors in this type of analysis include too high a temperature which may lead to removal of the element of interest (eg mercury and lead).
- Wet ashing (or digestion) uses oxidising acids to remove organic material. The process involves two to three hours boiling in concentrated sulfuric or nitric acid.
Dissolving acids
Various acids or combination of acids are useful in dissolving metals as shown in Table 1.4

Table 1.4  Common dissolving acids

<table>
<thead>
<tr>
<th>ACID</th>
<th>Formula</th>
<th>TYPICAL USES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric</td>
<td></td>
<td>Only used for readily oxidised metals such as iron and zinc, will not dissolve copper</td>
</tr>
<tr>
<td>Nitric</td>
<td></td>
<td>Will dissolve most metals, except chromium and aluminium</td>
</tr>
<tr>
<td>Sulfuric</td>
<td></td>
<td>Used for organic matter, but will dissolve many metals</td>
</tr>
<tr>
<td>Perchloric</td>
<td></td>
<td>Used for stainless steel and iron alloys that are not dissolved by other acids; explosive when heated in contact with organic matter</td>
</tr>
<tr>
<td>Hydrofluoric</td>
<td></td>
<td>The only acid which will dissolve silica-based materials, such as glass and silicate rocks; carried out in platinum or Teflon vessels</td>
</tr>
<tr>
<td>Aqua Regia</td>
<td>(3:1 nitric: hydrochloric)</td>
<td>Capable of dissolving the noble metals</td>
</tr>
</tbody>
</table>

Fluxing

- Used for difficult samples like silicate rocks, mineral oxides and some alloys
- Samples heated with various ionic salts (flux) to melting point in special crucibles
- Flux to sample ratio is usually 10 : 1
- Heating is maintained until the melt is without solid particles
- When cool water or dilute acid is used to dissolve the mixture

Table 1.5 lists some typical application of fluxes and crucibles

<table>
<thead>
<tr>
<th>FLUX</th>
<th>CRUCIBLE</th>
<th>SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>Nickel</td>
<td>Chromium ores</td>
</tr>
<tr>
<td>Na$_2$O$_2$</td>
<td>Nickel</td>
<td>Steel-making sinter and slag</td>
</tr>
<tr>
<td>K$_2$S$_2$O$_7$</td>
<td>Platinum</td>
<td>Beach sands</td>
</tr>
</tbody>
</table>
Available Techniques for Analysis

- Gravimetry
- Titrimetry
- Spectroscopy
- Chromatography
- Electrometry

Calculations

The subject Calibration and Data Handling was designed to provide a taster for the wonderful calculations ahead. You should keep the notes from this subject class close at hand. Chapter 5 from the notes will be invaluable to you as you consider things such as:

- The units of concentration
- Conversion between units
- Treatment of the data from analysis result to the final answer

In this text at the conclusion of each chapter you will find numerous concept questions and application type questions that you should attempt. (Your teacher will have available a complete set of answers for the latter).

QUESTIONS

Concepts

1. Why is matrix interference considered to be a problem in chemical analyses?
2. What is the method of matrix matching? What are its advantages and disadvantages?
3. Why would you use mg/L instead of g/L when reporting a particular result?
4. Why is the unit g/L not suitable for reporting the concentration of an analyte in a solid sample?

Applications

1. Describe how you would convert a value in mole/g to mg/kg
2. 25 mL of a sample is diluted to 100 mL and 5 mL of this further diluted to 250 mL and this sample analysed. What would the concentration of the analysed solution need to be multiplied by to obtain the concentration of the original sample?
3. A water sample was found to contain a cadmium level of \(10^{-7}\) M. Determine its concentration in (a) g/L, (b) g/100 mL, (c) mg/L and (d) ug/L. Which do you consider to be the most suitable unit?
4. Two new trainees analysed a standard sample to check their technique. The correct value for the sample was 0.105 M and accepted relative error in the technique is 3%. Given the following results for the two trainees, calculate:
   (a) their relative errors
   (b) their relative precision
   Did either trainee fail the accepted error test? Which trainee produced the more reproducible set of results
   Trainee 1: 0.117, 0.114, 0.113
   Trainee 2: 0.108, 0.097, 0.101
5. 10.0 mL of a sample was diluted to 250.0 mL and the concentration analysed to be 0.0952 g/L. what was the concentration of the original sample?
6. A 25.0 mL sample of vinegar was diluted to 100.0 mL and a 10.0 mL aliquot of this mixed with a reagent to form a coloured solution. This was accurately made up to 50.0
mL. The concentration of ethanoic acid (CH$_3$COOH) in this solution was determined to be 0.0295M. Calculate the concentration of the original sample in mole/L and g/100 mL.

7. A 10.0 mL sample of an industrial sample was analysed for zinc. It was diluted to 500.0 mL and a 5.0 mL aliquot of this further diluted to 100.0 mL. The concentration in the final solution was 1.02 mg/L. Determine the concentration of zinc in the original sample and convert this to a more suitable unit.

8. 8.381g of a sample of impure sodium carbonate was dissolved in 25.0 mL and a 5.0 mL aliquot diluted to 250.0 mL. 25.0 mL samples of this solution were analysed and found to have a concentration of analyte of 0.0567 M. Calculate the %w/w of the analyte in the original sample.

For each of the remaining questions calculate the concentration of the analyte in the sample and present the answer in a suitable unit.

9. 0.2997g of a sample was dissolved in about 50 mL of acid, 10 mL of a special reagent added and the solution made up to 250 mL. This solution was found to have an analyte concentration of 34.7 mg/L.

10. A 10.0 mL aliquot of sample was mixed with 5 mL concentrated acid, boiled down to about 5 mL and made up to about 75 mL. This was analysed and found to contain 7.481 x 10$^{-4}$ moles of analyte. The formula weight of the analyte is 207.

11. **Step 1** weigh accurately about 0.2g of sample into a beaker and dissolve in about 50 mL of 1M HCl

**Step 2** quantitatively transfer this solution to a 250.0 mL volumetric flask and make up to the mark

**Step 3** take a 10.0 mL aliquot of this solution and pipette into a 100 mL volumetric flask. Make up to the mark

**Step 4** analyse this solution

**Sample mass:** 0.2815g  **Analysis result:** 1.01 mg/L

12. Calculate the concentration of analyte in the squeezed juice as well as the orange

**Step 1** weigh the orange

**Step 2** squeeze all juice from the orange and measure the volume of juice

**Step 3** quantitatively transfer juice to 200 mL volumetric flask and make up to the mark

**Step 4** analyse 25.0 mL aliquots of this solution

**Mass or orange:** 156.5821 g  **Volume of juice:** 65 mL

**Analysis result:** 0.0728 moles/L  **FW:** 192

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**What you need to be able to do:**

- Differentiate between quantitative and qualitative analysis
- Explain the effect of matrix interference
- Explain how to compensate for matrix interference
- Be able to complete simple calculations involving unit conversions and basic stoichiometry