Analytical Science

A course (in 15 Chapters), developed as an Open Educational Resource, designed for use at 2nd year England & Wales undergraduate level and as a CPD training resource

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Description	Most samples require some form of sample pre-treatment/preparation, before analysis can be attempted. The sample preparation may involve either physical or chemical transformation of the analyte species and/or concentration/separation. This chapter compares the various of ways that these processes may be carried out and finally looks in more detail at the technique of solvent extraction.
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Chapter 3: Analytical Process Units 4&5 – Sample Preparation, Separation and Concentration

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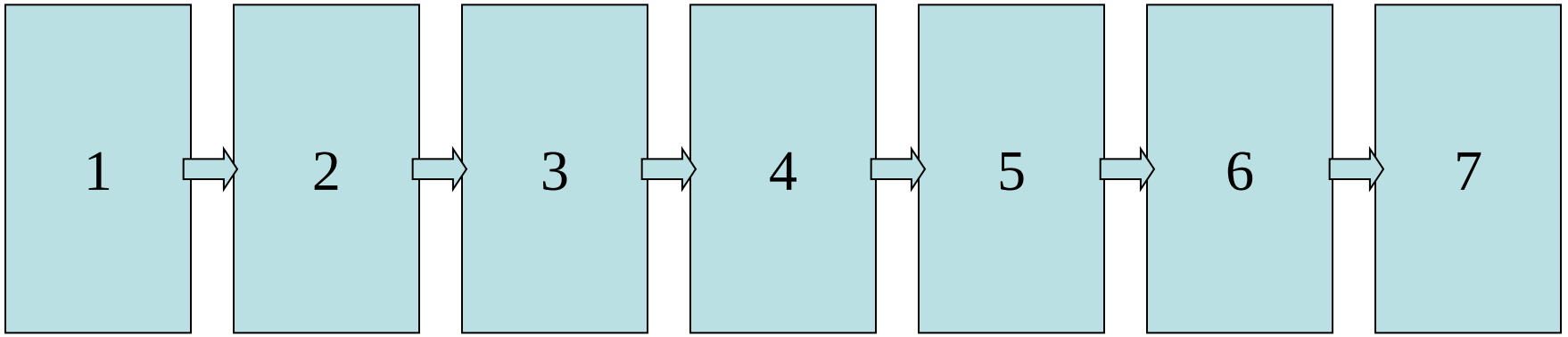
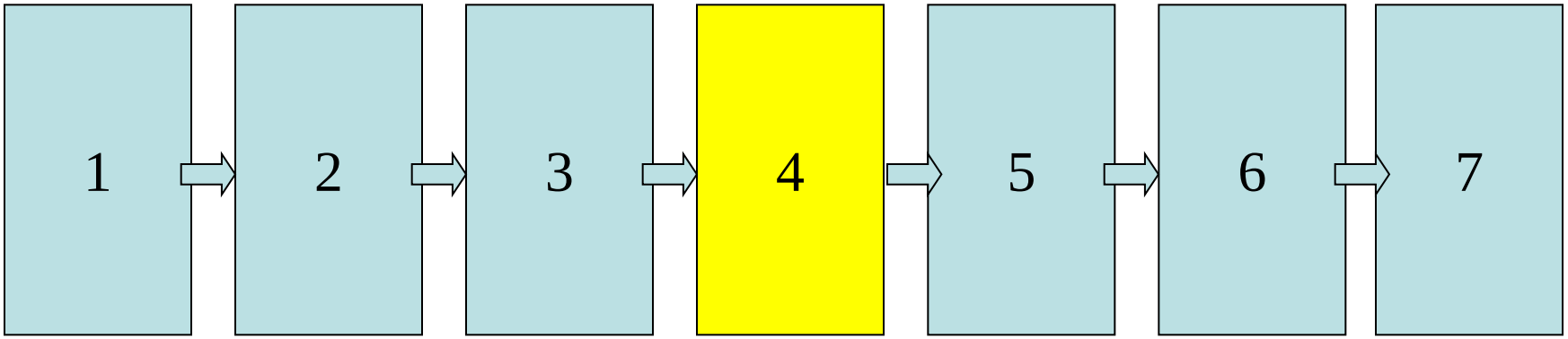
The analytical process model – revision slide

Any analysis may be considered as consisting of a maximum of seven unit processes. These are shown diagrammatically and descriptively below:



Unit 1. Consider the problem and decide on the objectives
Unit 2. Select procedure to achieve objectives
Unit 3. Sampling
Unit 4. Sample preparation
Unit 5. Separation and/or concentration
Unit 6. Measurement of target analytes
Unit 7. Evaluation of the data, have the objectives been met?

Process unit 4 – sample preparation



Although there are available, analytical methods that are capable of making analytical measurements directly on the sample taken, this is the exception rather than the norm. Most samples require some form of sample pre-treatment/preparation, before analysis can be attempted. The sample preparation may involve either physical or chemical transformation. Physical transformation may be simply crushing or grinding, whilst chemical transformation could involve:

- Dissolution in water or organic solvent;
- Treatment with dilute acids or bases;
- Oxidation with hot concentrated acids – often termed ‘wet oxidation’
- Treatment with molten fluxes at temperatures of up to 1400^{o}C

Sample preparation – preface

“Sampling and sample preparation are integral parts of the analytical process. They should be part of the analytical chemistry teaching curriculum, but often are not even mentioned during graduate or undergraduate analytical courses. The primary reason for this situation is that sample preparation is not considered a separate part of analytical science with its unique challenges, but rather the ‘thing’ you do when you develop and perform analytical methods.

The main difficulty in recognising the scientific principles of sample preparation is that the fundamentals of extraction, involving natural and frequently complex samples are much less developed and understood, compared to physicochemically simpler systems used in the separation and quantification steps of the analytical process, such as chromatograph and mass spectrometry. This situation creates an impression that rational design and optimisation of extraction for complex systems is not possible. Therefore, the development of sample preparation procedures is frequently considered to be an ‘art’ but not a ‘science’”.

Janusz Pawliszyn
Preface to ‘Sampling and Sample Preparation for Field and Laboratory’, J. Pawliszyn, Elsevier Science (2002).

Introduction

Whilst most analytical measurements are made on solutions, many samples requiring analysis are solid. Thus there is the need to be able to convert solids to a solution or other liquid state prior to measurements being carried out.

- **Dissolution** is the simplest option, provided the sample can be dissolved in a solvent that will not interfere with the analysis. Water is the solvent of preference for many analytical measurement techniques, however many organic compounds are insoluble in water and thus organic solvents also need to be considered. The use of solvents to extract the analytes from the sample matrix is also an option. This process is termed **solvent extraction.**
- Dilute acids and bases are also used, generally to dissolve samples with some opposite acidic/basic character.
- Many analytical problems require the measurement of trace inorganic content within organic matrices. This requires the removal of the organic material by a process of **wet oxidation** or **ashing**.
- Some inorganic matrices, particularly silicate based minerals, are virtually insoluble in normal solvents, acids or bases. In these cases, treatment with molten fluxes, termed **fusion**, at temperatures of up to 1400^{o}C is required.

Classification of techniques

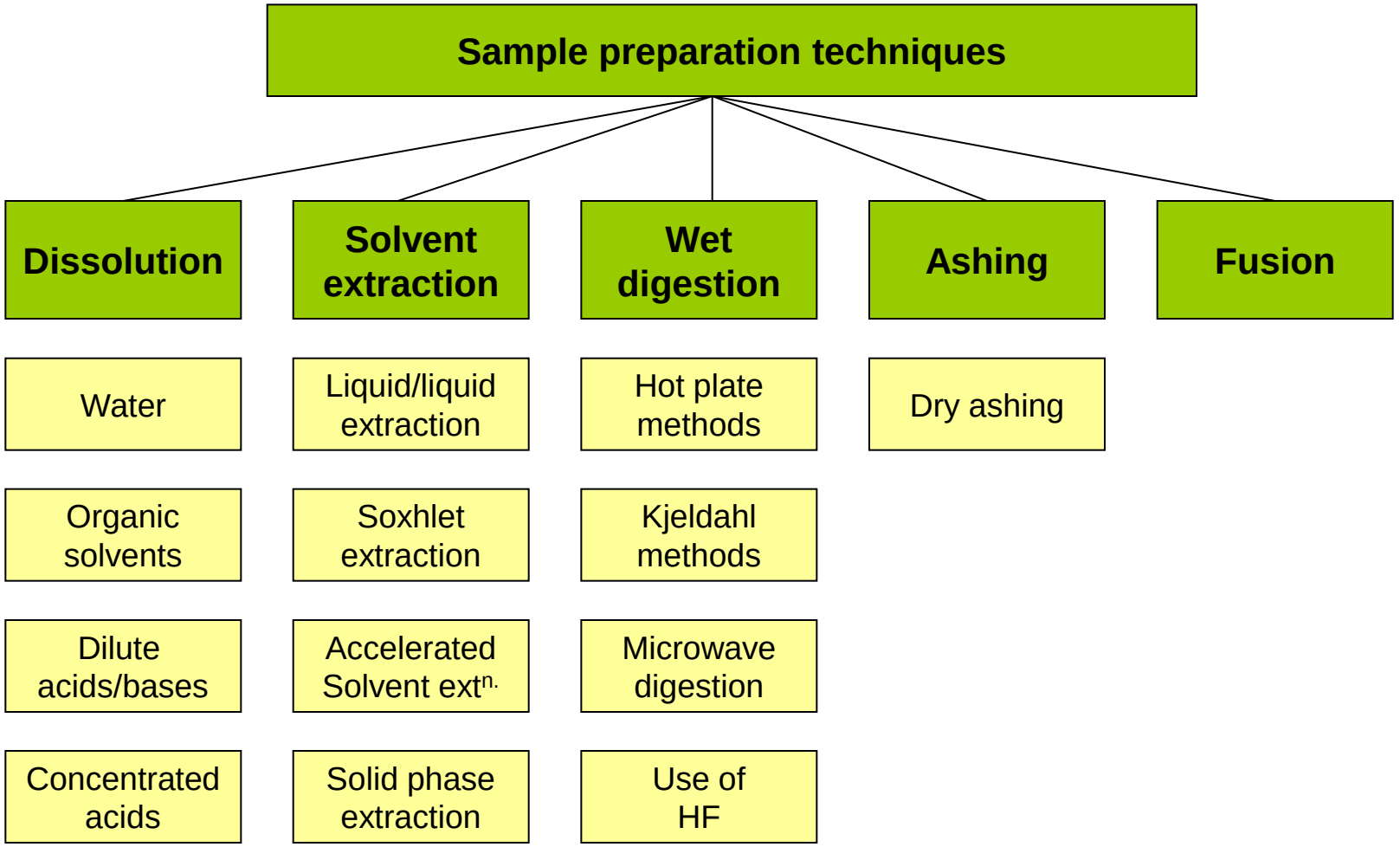


Figure 3.1 – classification of techniques

Fusion techniques

Many common substances, notably silicates and some mineral oxides, are attacked only slowly and in some cases not at all, in acid or alkali digestion methods. In such cases, a fused-salt medium is employed.

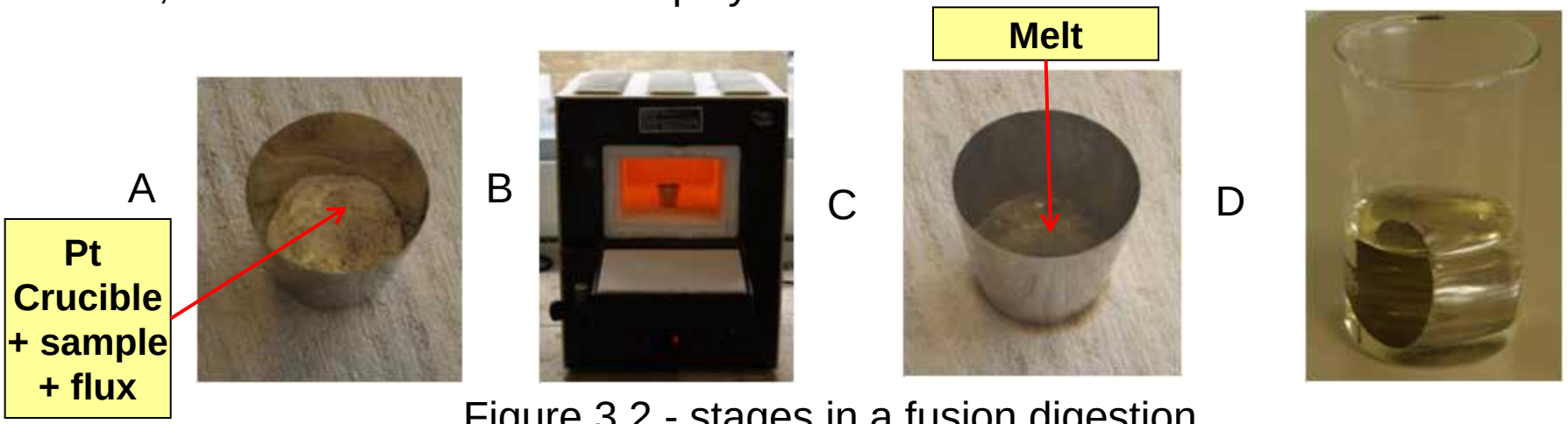


Figure 3.2 - stages in a fusion digestion

The sample as a fine powder is weighed into a suitable crucible and mixed in a ratio of 1:10 with a suitable pure inorganic material (flux) [A]. The combination is then heated to a very high temperature in a furnace [B], until a clear melt is apparent [C]. The time required may vary from minutes to hours. After cooling to room temperature, the crucible is placed in a beaker containing either water or dilute acid and warmed on a hotplate until the 'melt' dissolves [D]. Fluxes are capable of decomposing most substances by virtue of the high temperature required for their use and the high concentration of the reagent brought in contact with the sample. Table 3.1 on the next slide lists some typical fluxes, crucibles and types of materials that may be dissolved by using this procedure.

Common Fluxes

Flux	Melting point	Crucible	Applications
Anhydrous sodium carbonate[Na_2CO_3]	851	Pt	Basic flux for silicates; silica & alumina -containing samples; phosphates & sulphates
Lithium tetraborate [$Li(BO_2)_4$]		Pt	Powerful basic flux for silicates; most minerals; slags; ceramics.
Sodium hydroxide [NaOH]	318	Ni	Powerful basic flux for silicates; silicon carbide; certain minerals. (limitation is purity of reagent).
Potassium persulphate [$K_2S_2O_7$]	300	Pt or porcelain	Acidic flux for samples showing basic character (some metal oxides)
Boric oxide [B_2O_3]	577	Pt	Acidic flux for silicates and metal oxides where alkali metals are to be determined
Sodium peroxide [Na_2O_2]	380 decomposes	Fe or Ni	Powerful basic oxidising flux for sulphide minerals and some transition metal alloys

Table 3.1 – common fluxes used in fusion dissolution

Fusion techniques - disadvantages

- Given the large ratio of flux : sample that is required for a successful fusion, contamination of the sample by the flux occurs quite frequently. This is particularly a problem in trace metal analysis.
- The high dissolved salt content of the final aqueous solution, may cause difficulties in subsequent steps in the analyses.
- Due to the high temperatures required for successful fusion, losses of analyte may occur due to volatilization.
- Although certain types of crucible are recommended for particular applications [see table (1.1)], contamination of samples from direct attack on the crucible by the flux, frequently occurs. This is particularly the cases when using nickel crucibles.

Dissolution

Figure (3.1) lists four possible types of reagent that can be used to dissolve samples prior to analysis. This and the next 3 slides present some examples of where these particular reagents may be applied

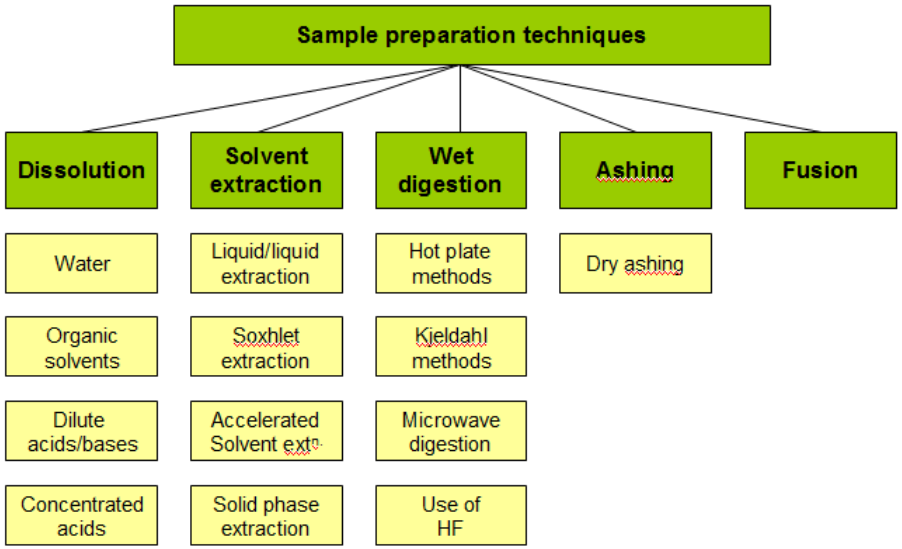


Figure 3.1 – Classification of techniques

Dissolution in water

To determine the purity of common water soluble reagents, or perhaps trace metal contamination within the reagent, the accurately weighed sample is dissolved in water. Dependent upon the reagent's solubility, it may be necessary to warm or heat the water to promote dissolution. No change in oxidation state will occur, however the sample will dissociate to form ions.

Examples: alkali metal salts (eg: Na_2CO_3, K_2SO_4, CsCl), most metal nitrates, many other metal salts (eg: $CuSO_4$) and organic substances which can ionise or hydrate (eg: citric acid).Remember that when the salt is formed between a strong base and a weak acid (eg: Na_2CO3), the resultant solution will have a high pH and thus may require neutralising with acid prior to analysis.

Dissolution in organic solvents

The vast majority of organic analyses are carried out in solution – chromatographic and spectroscopic techniques are good examples. However, although most organic substances are soluble in a range of organic solvents, the solvent of choice must be the one that does not interfere with the measurement technique.

Example: for analysis in the ultra-violet (UV) range of the electromagnetic spectrum, the solvent of choice would be one that did not exhibit strong UV absorption characteristics – methanol, ethanol and acetonitrile are good examples.

Note: more detailed information on solvent choice for use in chromatographic and spectroscopic procedures can be found in Chapters 7 & 11 respectively in this teaching and learning programme

Dissolution in dilute acid/bases

Many common reagents which are used across a wide range of industries are insoluble in water and thus require dissolution in acids or bases to effect solubility. No change in oxidation state is expected to occur, however when using nitric acid which is an oxidising acid, a change in oxidation state may occur in some circumstances.

Example: calcium carbonate, which is used as a filler in a wide range of plastics and pharmaceuticals would need to be dissolved in dilute hydrochloric acid in order to assay for purity or test for trace metal contaminants

$$CaCO_3 + 2HCl \rightarrow Ca^{2+} + 2Cl^- + CO_2 + H_2O$$

The choice of acid can be important. In the example given above, dilute nitric acid could be used as an alternative to hydrochloric, but not sulphuric acid, because calcium sulphate is only slightly soluble in aqueous solutions.

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$$

Dissolution in concentrated acids

The acids most frequently used in this context are hydrochloric and nitric acids or a 4 volume : 1 volume combination of the two to produce 'Aqua-Regia'.
In many instances the analyte is oxidised to a higher oxidation state except with organics where protonation may occur.

Example: dissolution of metals and alloys, prior to analysis by chemical or spectroscopic methods. The acids required for dissolution relate to the relative positions of the metals in the electrochemical series
http://en.wikipedia.org/wiki/Standard_electrode_potential_(data_page)
Copper for instance requires dissolution in nitric acid, whilst zinc may be dissolved in hydrochloric acid.

$Zn + 2HCl \rightarrow Zn^{2+} + 2Cl^-$ [The H^+ is acting as the oxidising agent]
$Cu + 4HNO_3 \rightarrow Cu^{2+} + 2NO_3^- + 2NO_2 + 2H_2O$

Nobel metals (Au, Pt & Pd for example) require dissolution in 'aqua-regia'. This mixed acid reagent, on heating produces nitrosyl chloride [NOCl] and chlorine and will attack many substances not attacked by other acids.

$3HCl + HNO_3 \rightarrow 2H_2O + NOCl + Cl_2$

Solvent extraction

There are numerous occasions when it becomes necessary to remove the target analyte from the sample matrix, before analysis can be carried out. The reason for this is either that:

- The sample matrix cannot be analysed directly or would interfere with the measurement process;
- The level of analyte is too low for direct analysis and thus requires concentrating prior to measurement.

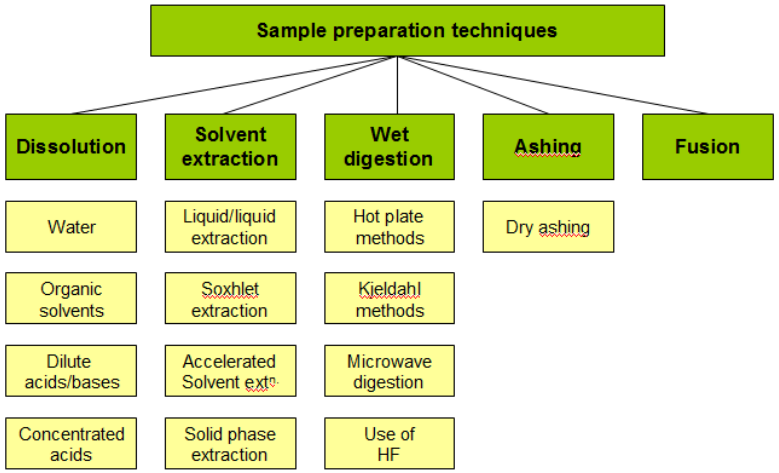


Figure 3.1 – Classification of techniques

Figure (3.1) recommends four different methods for the extraction target analytes from both solid and liquid sample matrices. These are:

- **Liquid/liquid extraction** – extract target analytes from a liquid sample matrix
- **Soxhlet extraction** – remove target analytes from a solid sample matrix
- **Accelerated solvent extraction** – a high pressure and more rapid version of the Soxhlet type extraction;
- **Solid phase extraction** – concentrate target analytes from a solution matrix

Liquid/liquid extraction

Note a more detailed coverage of liquid/liquid extraction may be found later in this Chapter

Extraction using organic solvents is the most common extraction technique for separating a soluble analyte from a liquid sample. The technique is based on the distribution of the analyte between two immiscible liquids, one of which is normally aqueous. The important parameter for good extraction yield is the **distribution coefficient** of the analyte between the two phases involved.

Definition of "Distribution Coefficient"

This may be defined as the quantitative distribution at equilibrium, of a solute (analyte) between two immiscible phases. The higher the value of the coefficient, the better the transfer of the solute from the sample (aqueous) to the extracting (organic) phase

A distribution coefficient can usually be influenced advantageously by establishing a specific pH, thus dividing the sample into strongly or weakly acidic, neutral, or basic fractions. If the distribution coefficient is large, the simplest method for liquid-liquid extraction is shaking the sample with a suitable amount of an immiscible organic solvent. However, with small distribution coefficients or with large sample volumes, continuous extraction or counter-current extraction is necessary to attain a complete separation.

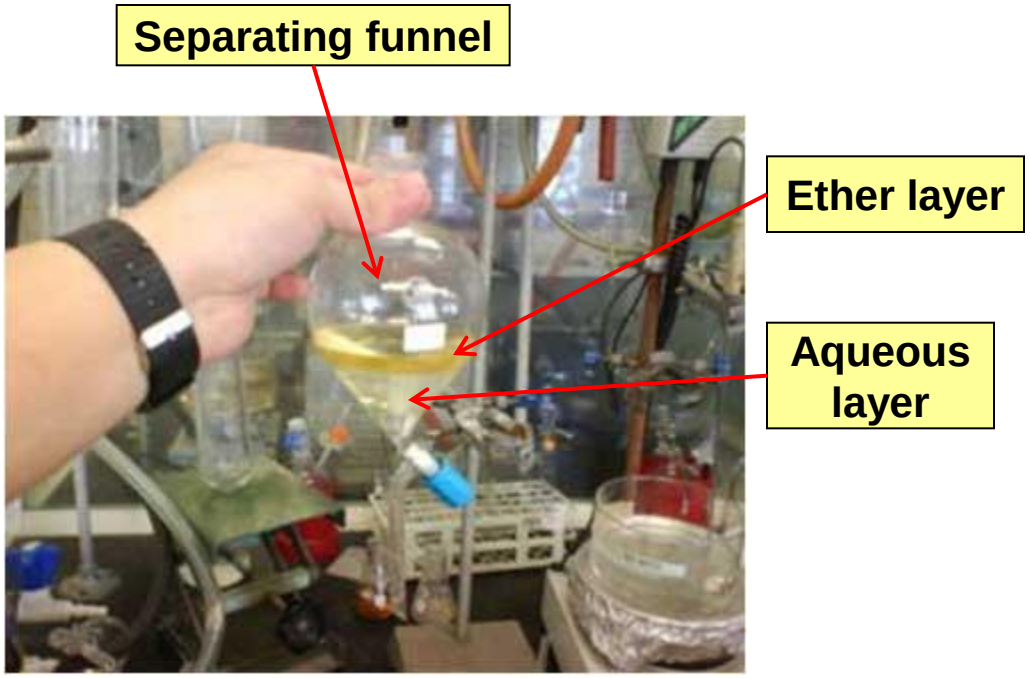


Figure 3.3 – solvent extraction

Procedure for solvent extraction

To an aqueous sample, present in a separating funnel, add a smaller volume of a suitable immiscible organic solvent. Stopper the flask and shake thoroughly to promote mixing of the two liquids. With very volatile solvents, it will be necessary to release the stopper to release pressure inside the flask once or twice during the extraction.

After allowing the phases to separate (figure 3.3), separate the two layers and if required, repeat the extraction with a further aliquot of organic solvent. Combine the organic phases and reduce in volume to concentrate the analyte for eventual analysis.

The most convenient solvents to use are those with higher densities than water, however these tend to be chlorinated hydrocarbons, which due to their toxicity are gradually being faded out. Aliphatic ethers, esters and higher molecular weight ketones are now popular.

Soxhlet extraction

This mode of extraction is used to remove organic substances of low volatility from complex solid matrices such as soil or plant materials.

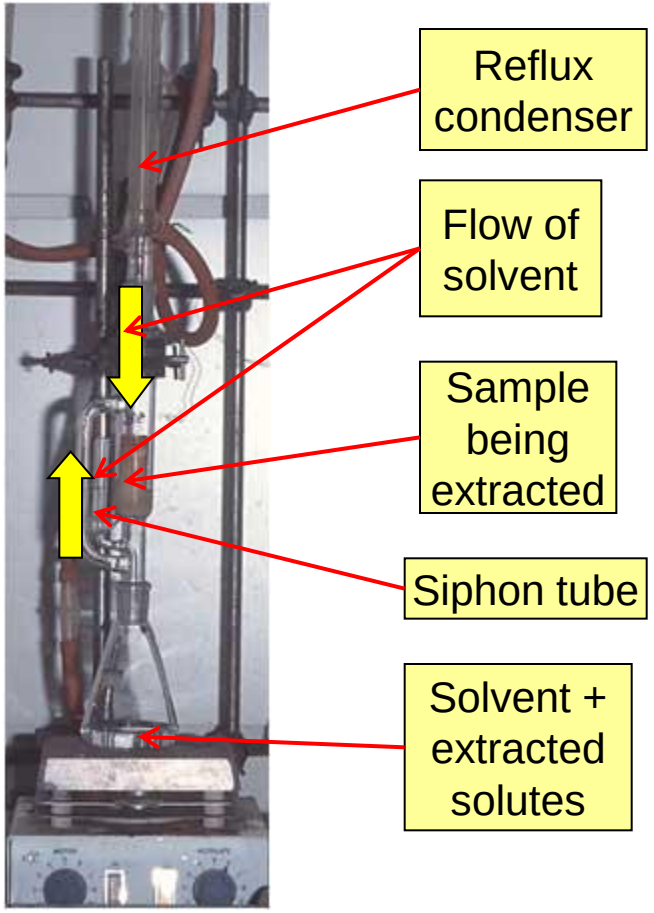


Figure 3.4 – typical Soxhlet extraction

A typical piece of Soxhlet extraction equipment is shown in figure (3.4). The sample to be extracted is weighed into a cellulose thimble and placed in the extractor. A reflux condenser is attached to the top of the extractor and a flask of solvent is attached at the base. The solvent is then heated to boiling. The hot solvent vapour condenses on the reflux surfaces and the hot solvent then drops back onto the sample. When the chamber containing the thimble is full of solvent, it automatically siphons back into the flask, taking with in the extracted solutes. The process is allowed to continue until it is considered that all extractable substances have been removed. In some instances this could take 24 hours or more. The apparatus is then dismantled and the solvent evaporated to a volume suitable for analysis.

Accelerated solvent extraction

Accelerated solvent extraction (ASE) uses conventional solvents at elevated temperatures (100-180˚ C) and pressures (1500-2000 psi) to enhance the extraction of organic analytes from solids. Figure (3.5) shows a typical instrumental arrangement for an ASE system. Unlike the two previous extraction procedures that have been described, this system is totally automated. The sample is weighed into the extraction cell and the solvent(s) for extraction are chosen as are the extraction times. The extraction can be completed in a relatively short period of time and as shown in figure (3.6), a number of samples can be extracted sequentially.

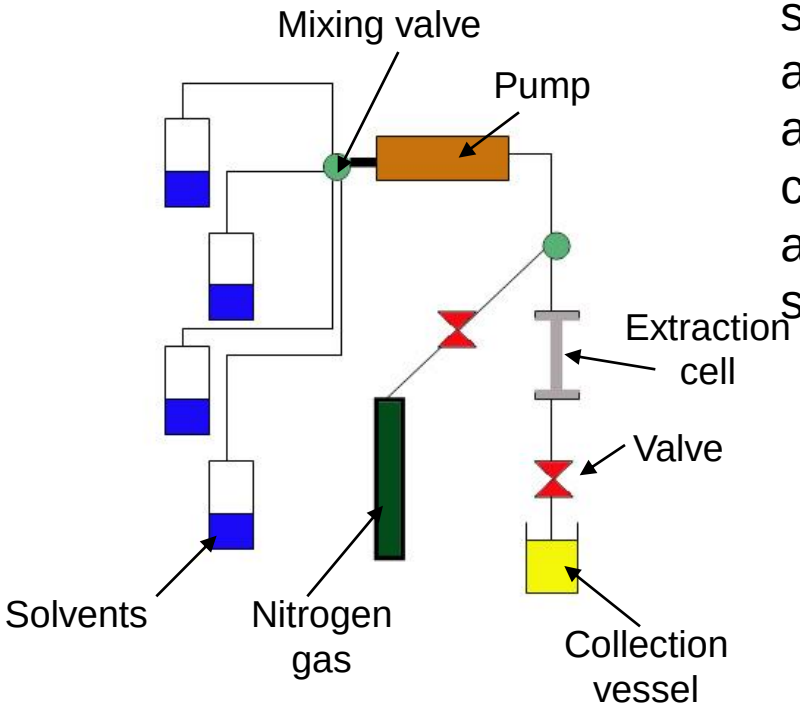


Figure 3.5 – schematic diagram of A Dionex ASE system

Figure 3.6 - Dionex ASE instrument

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Although ASE systems are far more expensive and sophisticated than conventional extraction systems, they do offer significant advantages in terms of extraction performance, time and volumes of solvents employed. The advantages include:

- The high pressure increases the solvent boiling point; therefore, the extraction is conducted at higher temperatures.
- The solvent penetrates deep into the sample matrix, thus facilitating the extraction of analytes trapped in matrix pores.
- The higher temperatures increase analyte solubility and weakens the solute-matrix bonds thereby making the mass-transfer a much faster process.
- The high temperature and pressure reduces the solvent viscosity and surface tension, which improves solvent penetration into the matrix.
- The volumes of solvent used are much smaller – generally no more than 50 cm^3.

Figure 3.7 - stainless steel extraction cell

Overall these conditions produce quicker extractions and enhanced analyte recovery. Figure (3.7) shows a typical extraction cell.

Solid phase extraction

Solid-phase extraction (SPE) is a powerful sample pre-treatment procedure, particularly prior to analysis by high performance or gas-liquid chromatography. It involves the exhaustive removal of chemical substances from flowing samples (often aqueous), via retention onto a solid sorbent contained in a preformed cartridge. The adsorbed substances are subsequently recovered by selective elution from the sorbent and the resultant solutions can then be analysed by the appropriate chromatographic technique.

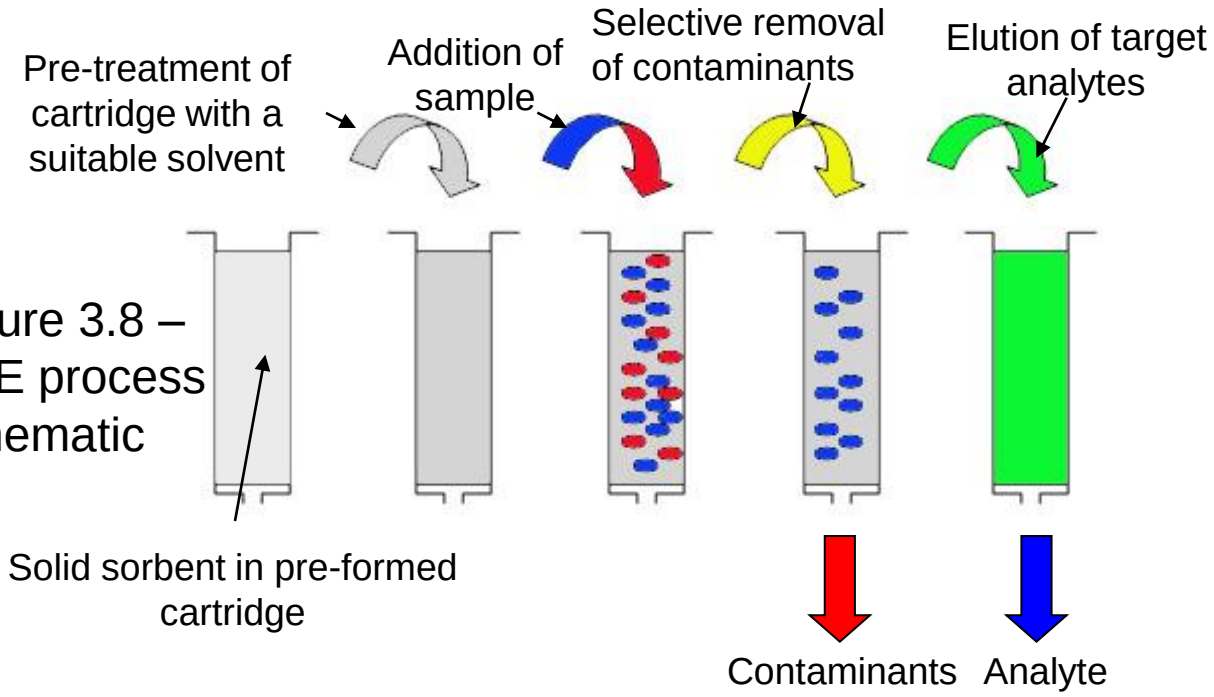

Figure 3.8 – SPE process schematic

Figure (3.8) shows the generic process used in solid phase extraction. The volume of sorbent used is normally not more than 2 cm^3 and this is contained in a small polypropylene syringe. The target analyte often initially present in a **large** volume of water, is eventually eluted in a **small** volume (1 cm^3) of a suitable volatile organic solvent.

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Note: further coverage of this topic can be found in at the end of this chapter

Solvent extraction – comparison of methodologies

Method	Advantages	Disadvantages	Applications
Liquid/liquid extraction	▪ Requires only basic laboratory glassware	▪ High dilution of the extract ▪ High solvent consumption	▪ Recovery of semi-volatile organics from liquid matrices – mainly water
Soxhlet extraction	▪ Requires only traditional laboratory equipment	▪ Long extraction times ▪ Large volume solvent consumption	▪ Recovery of organics, other than volatiles, from solid matrices
Accelerated solvent extraction	▪ Small volumes of solvent used ▪ Fast extraction ▪ Good extraction efficiency ▪ Concentrated extracts	▪ High cost of specialist equipment	▪ Recovery of organics, other than volatiles, from solid matrices
Solid phase extraction	▪Uses only small volumes of organic solvents ▪ Provides a concentrated sample for analysis	▪Requires specialised equipment	▪ Recovery and concentration of semi-volatile organics from liquid matrices.

Table 3.2 – comparison of solvent extraction methodologies

Sample preparation – wet digestion

Wet digestion is used, to destroy organic components of a sample matrix in preparation for the analysis of the inorganic analytes. The technique is most frequently used as a precursor to trace metal analysis, in for instance, the food industry. The digestion is brought about by boiling the sample with concentrated mineral acids – sulphuric, nitric and perchloric can all be used. In some methods and with some matrices, it is necessary to use a combination of acids, sulphuric and nitric being the most usual combination. The chemistry of such a process is shown below

Organic matrix + c H_2SO_4 → CO_2 + SO_2 + C + metal sulphate(s)

c HNO_3 or H_2O_2

CO_2

Note: sulphuric acid should not be used for the analysis of metals which form sparingly soluble sulphates for instance Ca, Sr , Pb & Ba

Note: because of the potential explosive nature of products produced when perchloric acid is boiled with organic matrices, this reagent should only be used in combination with other the acids and then only employed by operators experienced in handling this reagent.

Hot plate heating

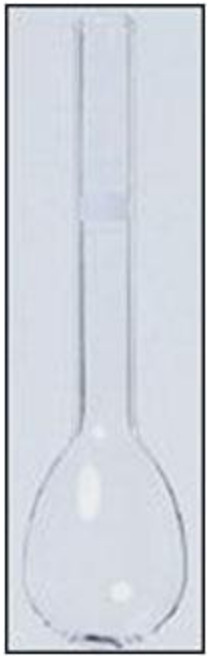
This is the simplest form of acid digestion. The sample is weighed into a beaker to which is then added concentrated nitric acid. The beaker is loosely covered by a watch glass and placed on a hotplate in a fume cupboard. The acid is then boiled gently to digest the sample. Further portions of nitric acid may be required for resilient samples. Once the digestion is complete (no further fumes of oxides of nitrogen are apparent), the digest is gently evaporated to near dryness and the residue then dissolved in dilute acid, in preparation for analysis.

Although this is the simplest of the acid digestion procedures, many biological matrices are incompletely digested using this procedure, as the temperature of the boiling acid is too low. Two alternative procedures may be used to overcome this problem:

- Digestion using Kjeldahl apparatus;
- Digestion using microwave heating.

Kjeldahl flask method

The Kjeldahl method of analysis refers to the method developed by Johann Kjeldahl for the determination of the nitrogen content of proteins. The initial digestion of the protein was carried out in a long-necked pear shaped flask, similar to that shown in figure (3.9). The long neck on the flask acts as an air condenser, enabling the concentrated sulphuric acid to be boiled vigorously and for the resultant sulphur trioxide (SO_3) to reflux on the wall of the air condenser.



These flasks are also used to digest organic substances prior to analysis for metal contents – hence the name 'Kjeldahl flask method'. Any carbon not evolved as carbon dioxide will appear as finely divided carbon, giving the digest a black appearance. This may be removed by the careful addition of pure concentrated nitric acid or 100 volume hydrogen peroxide to the hot sulphuric acid in the flask. When all of the carbon has been removed a clear solution will result. After cooling, the digest is transferred to a volumetric flask for eventual metal analysis.

Note: this process must be carried out in a fume cupboard.

Figure 3.9 – typical Kjeldahl Flask

Microwave digestion

For an introduction to Microwave Chemistry read the following WEB article: http://en.wikipedia.org/wiki/Microwave_chemistry

Water is an excellent absorber of microwave energy and thus aqueous solutions lend themselves to heating by using this technology. Initially, attempts were made to modify 'kitchen' type microwave ovens to carry out digestions in sealed plastic containers (termed bombs), however control of the energy was difficult to reproduce, making it difficult to replicate digestion conditions. Laboratory microwave ovens were therefore developed, which allowed multiple digestions to be performed under controlled conditions. Figure (3.10) shows a modern commercial microwave digestion oven.

Figure 3.10 – microwave oven

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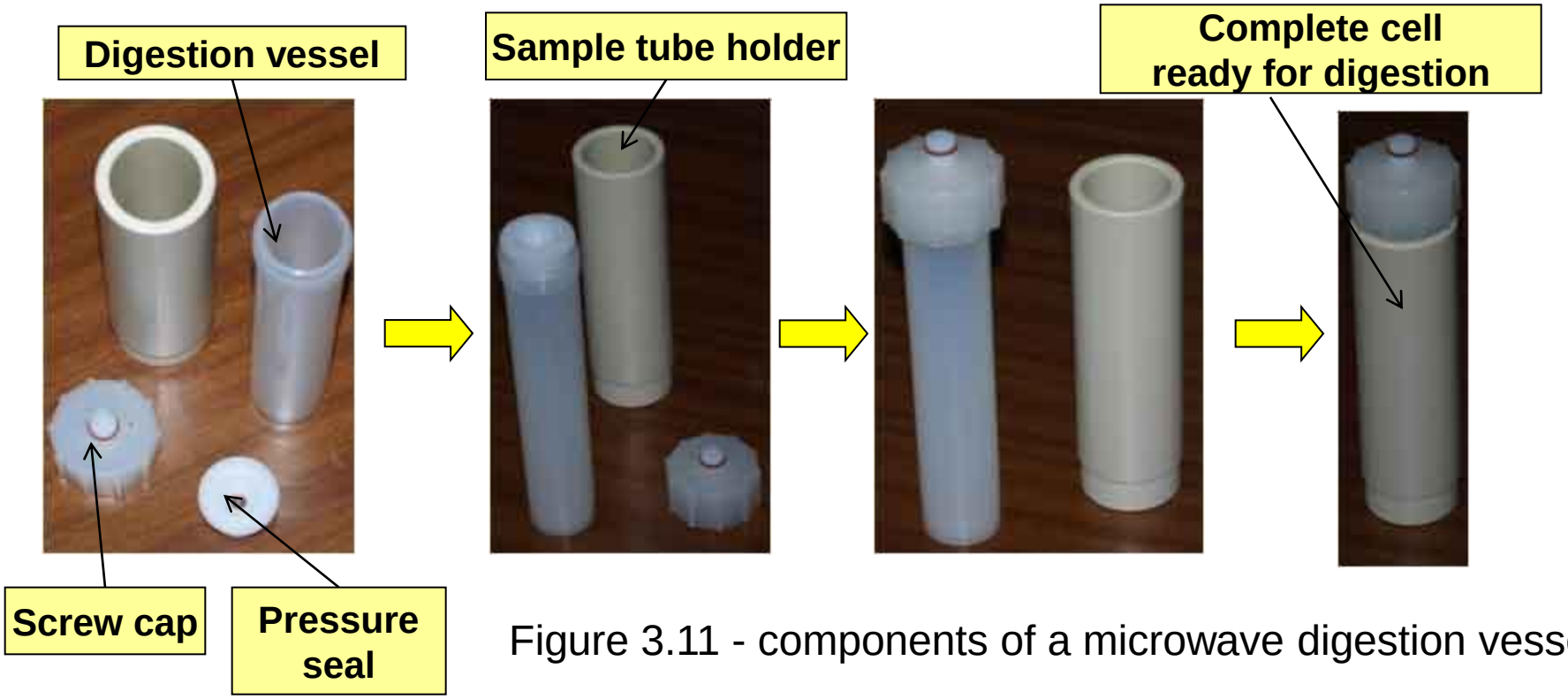


Figure 3.11 - components of a microwave digestion vessel

The small quantity of sample (< 1g) is weighed into the plastic (Teflon PFA) digestion vessel to which is added an aliquot of conc. nitric acid (5-10 cm^3). The vessel is then assembled, placed in the microwave oven, the door closed and conditions for digestion set on the instrument panel. Once digestion is complete which should take no more than 30 minutes, the vessel is cooled to room temperature before opening. The contents are then transferred to a volumetric flask for eventual analysis.

There are a number of advantages offered by microwave digestion over traditional methods

- Nitric acid can be used on its own due to the high pressures induced in the sealed vessel.
- There is less chance of volatile metal species being lost during the digestion.
- A number of similar digestion may be performed simultaneously.
- The process is much faster and less labour intensive.

Use of Hydrofluoric acid

Hydrofluoric acid (HF), is a useful reagent for the removal of silicates, prior to the analysis for other metallic elements. The sample is weighed into a platinum crucible, similar to that shown in figure (3.2A) on slide 8. The crucible is placed on an electric hotplate inside a fume cupboard and to it is added a small quantity of concentrated sulphuric acid (sufficient to wet the sample) together with a few cm^3 of concentrated HF. A platinum lid is then placed loosely on the crucible such as to allow loss of gases and the crucible is then gently heated. The HF reacts with the silicate to form volatile silicon tetrafluoride (SiF_4). Further aliquots of HF are added until all of the silicate has been removed. The sample is then gently evaporated to dryness and the residue dissolved in dilute nitric or hydrochloric acids for eventual analysis of other metallic elements.

$$SiO_2 + 4HF \Rightarrow SiF_4 + 2H_2O$$

Although it is preferable to add a small quantity of sulphuric in addition to the HF, this should be avoided when analysing for metals which form only sparingly sulphates.

Note: concentrated HF is a very toxic and corrosive reagent and should be used only in the presence of operatives familiar with this reagent.

Dry ashing

Figure 3.12 – typical small muffle furnace

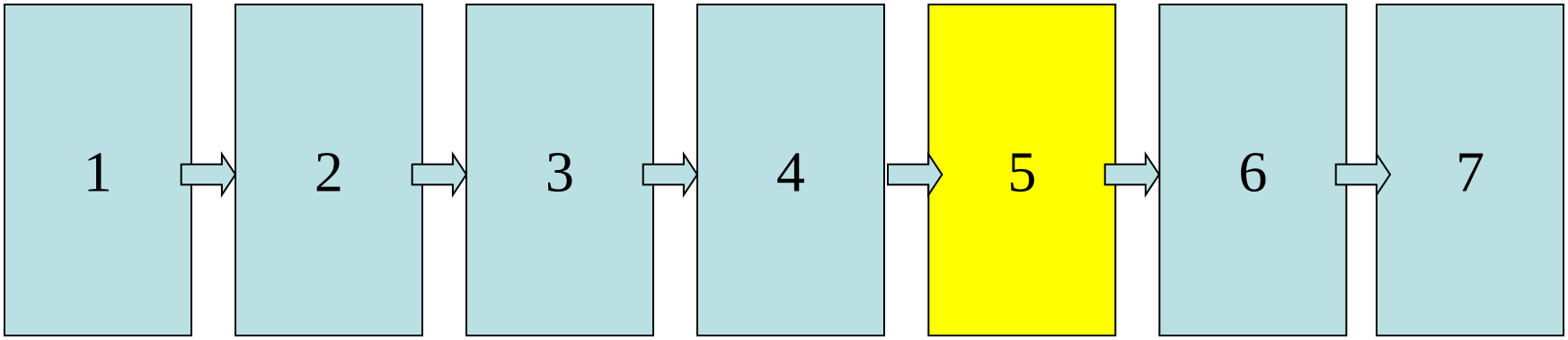
This method of destroying carbonaceous matter from samples prior to analysis for non-volatile metals, is the simplest and safest to carry out. The sample is weighed into a crucible (silica, porcelain and platinum may all be used) and placed in a small muffle furnace, similar to that shown in figure (3.12). The temperature of the furnace is then allowed to heat up to between 400-500^{o}C and then held at that temperature until all of the organic material has been destroyed by air oxidisation to carbon dioxide. Dependent upon the sample, this could take several hours to complete. A residue of metallic oxides remains which may then be dissolved in concentrated nitric acid. The choice of temperature for ashing depends upon the metals being targeted for analysis – some being more volatile than others. If some of the residue is silica (SiO_2), this can then be treated with HF as described on the previous slide. For certain types of sample, it is recommended that sulphuric acid or magnesium oxide is added to the sample, prior to ashing to help retain potentially volatile elements, however any additions could cause sample contamination. Care must be taken to avoid the sample igniting during the ashing process as this will lead to losses of the analytes within the smoke particles.

Comparison of methodologies for destruction of organic matrices

Method	Advantages	Disadvantages	Applications
Dry ashing	▪ Can handle large samples ▪ Uses normal laboratory equipment	▪ Possible volatilisation of some elements and contamination from airborne dust ▪ Slow	▪ Metal in foodstuffs – Pb, Cu, Cd, Zn & Fe ▪ Nutritional elements in foods: Fe, K, Ca, Mg, Mn
Wet digestion - Hot-plate method	▪ Uses standard glassware ▪ HNO_3 most used oxidant although other mixtures of acids & oxidants have been reported	▪ Labour intensive ▪ Slow ▪ Losses of volatile elements may occur	▪ Suitable for some biological matrices – see reported data ▪ Can be used to extract metals form soils
Wet digestion - Kjeldahl method	▪ Uses inexpensive laboratory glassware ▪ H_2SO_4 capable of digesting most organic matrices	▪ Labour intensive ▪ Analysis solution strong in H_2SO_4 ▪ Losses of volatile elements may occur	▪ Most organic matrices for analysis of metals that form soluble sulphates
Microwave digestion	▪ HNO_3 can be used alone ▪ Multi-sample digestion ▪ Fast process and less labour intensive ▪ Suitable for analysis of most metals	▪ Requires expensive dedicated equipment ▪ Only small sample weights can be digested	▪ Suitable for most organic matrices – particularly those of biological origin. ▪ Can be used to extract metals from soils

Table 3.3 – comparison of methods for the destruction of organic matrices

Process unit 5 – separation & concentration



Separation of the analyte from the other components in the sample matrix and/or **concentration** of the analyte both prior to analysis are frequently required in many of the complex analyses that need to be carried out in the 21st century. **Separation** is required to avoid interference from other components in the sample. **Concentration** is required as analytical techniques are not always available to measure analytes down to the levels required by either legislation or sample providers. The methods used to perform these functions can be the same, hence their combination in this process unit. In some instrumental technologies, highly efficient separation occurs automatically as part of an overall analytical system, in others, separation and concentration are carried out prior to the final analytical measurement.

Classification of methods & techniques employed

Methods and techniques that can perform both separations and/or concentrations have already been introduced earlier in this chapter and include:

- **Solvent and Soxhlet extraction**. Although these were initially manual procedures some automated versions have been developed.
  Concentration of extracted analytes generally occurs via evaporation of the extracting solvent in one of three ways:
  - Slow evaporation on a hot-plate or on a water bath
  - Gas-blowdown - the solvent is evaporated on a water bath under a stream of nitrogen gas. This will avoid possible oxidation of the analyte.
  - Using a rotary evaporator. Useful when large volumes of solvent need to be removed
- **Accelerated solvent extraction**. Because of the high pressures associated with this procedure, this method needs to be fully automated. Due to the very efficient nature of the extraction only small volumes of solvent are required, hence concentrated extracts are obtained.
- **Solid phase extraction.**

These forms of separation and concentration techniques, are generally employed when organic analytes are required to be measured in solid or aqueous matrices.

Analytical methods where separations are part of an overall analytical system

These are essentially chromatographic, electrophoretic and mass spectroscopic systems and are used for direct analysis of components present in organic and aqueous solutions. Dependent upon the technique used for measurement, analytes can be either organic or inorganic in nature. [**Extensive coverage of these techniques may be found in Chapters 6,7,8 & 13 of this teaching and leaning programme**]. For example, with instrumental chromatographic techniques the generic separation and analysis process can be illustrated as shown in figure (3.13)

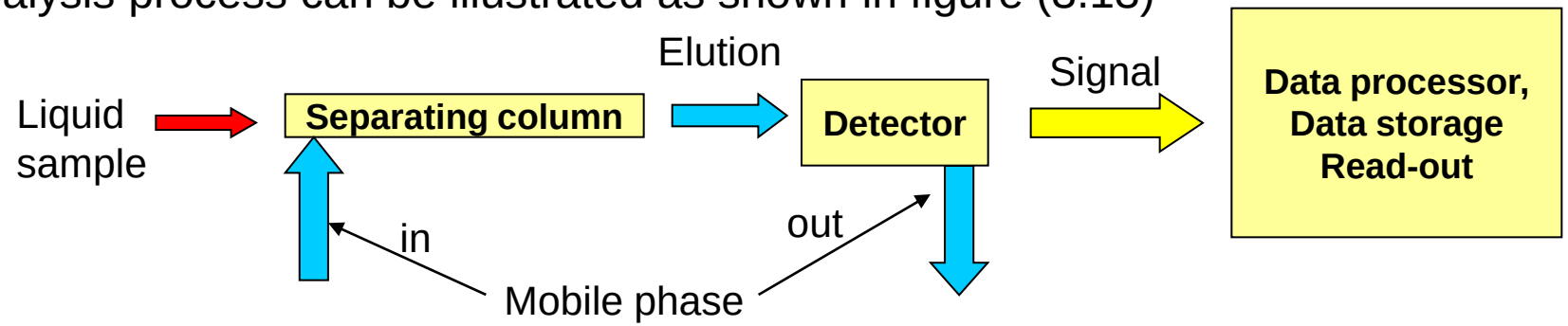


Figure 3.13 – schematic diagram showing fundamentals of chromatographic analysis

The liquid sample is introduced into the chromatographic column and mixed with the mobile phase. Separation of the various components in the sample then occur as they move along the column towards the detector. These then elute separately into the detector which generates a signal based upon the quantity of substance eluted.

The detector shown in figure (3.14) generally measures **eluates** (those substances eluted from the separating column) based upon their spectroscopic or electrochemical properties. Popular detectors for measurement of organic substances are **ultra-violet detectors (fixed wavelength and diode array)** and **mass spectrometers**. For the measurement of inorganic ions, popular detectors include **photomultipliers**, **mass spectrometers** and **electrochemical** detectors based upon measurements of conductance and of current. For many applications nowadays, mass spectrometers are the detectors of choice, as they are able to provide an additional layer of separation to that provided by the chromatography column.

.

Figure (3.14) shows a typical gcms (gas chromatograph/mass spectrometer). The components of the mixture separated by the gc can be both uniquely identified and quantified by the spectrometer.

Figure 3.14 – typical gas chromatograph with mass spectroscopy detector

Separation & concentration - reflection

- Separation is frequently required before measurements can be performed on a sample due to:
  - The sample not being in a suitable state for measurement (solid sample with a liquid measurement technique)
  - Other components in the sample cause interference in the measurement technology
- Concentration of the analyte is required when detection techniques available to the analyst are insufficiently sensitive to measure at the level required. Concentration is effected by careful solvent evaporation.
- Some techniques perform both functions simultaneously – ASE and SPE
- Many instrumental techniques perform separation as part of the overall analytical system – GC, HPLC, IC, CE, mass spectrometry. Mass spectrometry detectors when employed in GC, HPLC and CE, add an extra level of separation such that lower separation efficiencies can be required by the initial chromatographic or electrophoretic separation

Additional notes and discussion on the techniques of:

- Solvent Extraction;
- Accelerated Solvent Extraction

Introduction

Solvent extraction is a rapid way of separating inorganic or organic analytes, or solutes.

The solutes distribute themselves between two immiscible liquids or phases. Most commonly, solutes are extracted from an aqueous phase into an organic phase. As organic solvents are not generally good solvents for ionic species, a neutral species is usually extracted, for example metal ions are reacted with chelating agents that neutralise the charge and make the ion ‘organic like’.

For more difficult separations multiple extractions are performed the theory of which helps explain chromatographic procedures.

Solvent extraction is used to:

- Remove interfering species prior to measurement;
- Pre-concentrate analytes prior to measurement
- Produce a measurable form of an analyte species.

For solvent extraction a separating funnel is used as illustrated in figure (3.15)

The solute (S) and extraneous compounds are dissolved in a suitable solvent (e.g. water) which is poured into the separating funnel, a second immiscible solvent is added and the funnel shaken to allow equilibrium to develop.

The phases are allowed to separate and with the correct choice of solvents, the solute of Interest will be in the extracting solvent, while the extraneous compounds will remain in the original solvent phase.

In most solvent extractions, one of the phases is normally aqueous.

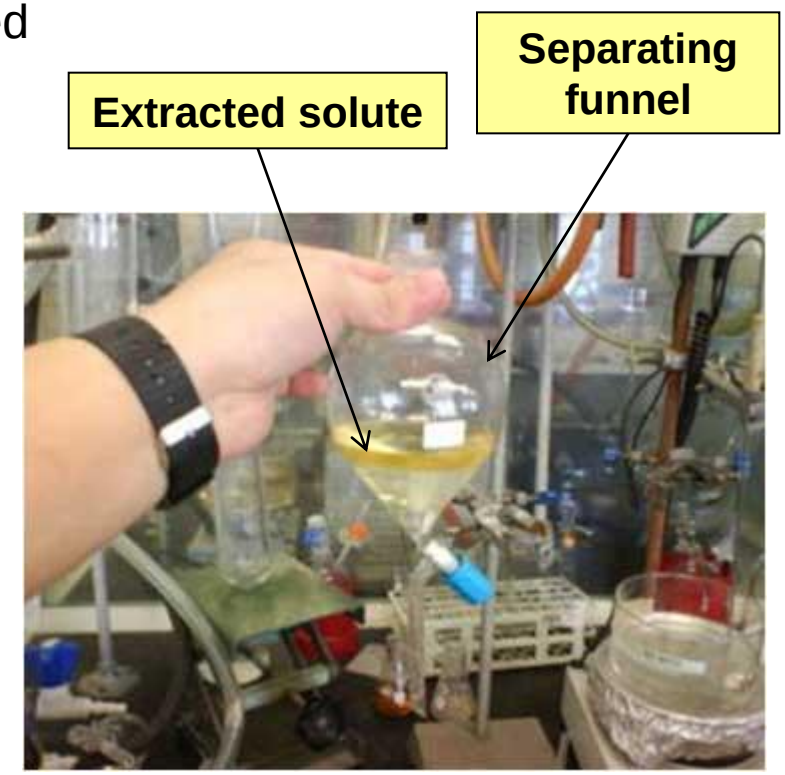


Figure 3.15 - a separating funnel and immiscible solvents

The distribution coefficient

A solute ‘S’ will distribute itself between the two immiscible phases according to its distribution coefficient, K_D.

$$K_D = \frac{[S_1]}{[S_2]} \qquad \text{Equation (3.1)}$$

Where $[S_1]$ is the concentration of the solute in the first solvent eg an organic solvent and $[S_2]$ is the concentration of the solute in the second solvent eg water. If K_D is very large the bulk of the solute will be present in solvent 1. This is the preferred scenario when extracting a solute from an aqueous solution into an organic solvent.

Extraction of weak acids (or bases)

Many substances are partially ionised in aqueous solutions if they are weak acids or bases. This means that these solutes exist in two forms the **ionised** and the **non-ionised species**. An equilibrium exists between these two forms which is pH dependent.

Consider a weak acid:

$$HA \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + A^-$$

Equation (3.2)

The ionised species will readily partition into the aqueous layer, as water itself is partially ionised, whereas the non-ionised species will readily partition into the organic layer. **Remember 'like dissolves like'.**

When dealing with aqueous species, the solute may exist in equilibrium with a number of other forms only one of which may extract into the organic phase.

Figure (3.16) below gives the example of a weak acid

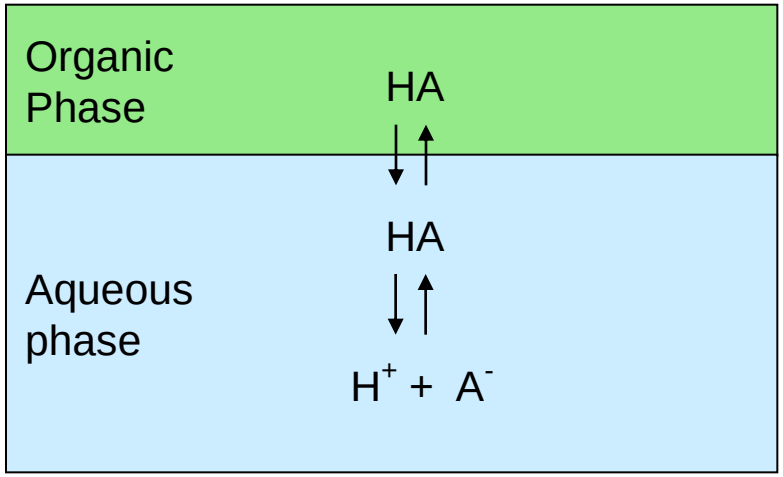


Figure 3.16 partitioning between an organic phase and an aqueous phase of ionised and non-ionised species

This means that not all of a weak acid (or base) will be extracted from an aqueous solution (*aq*) into an organic solvent (*org*) as, K_D, the **distribution coefficient (or partition coefficient)** only takes into account one of the species

$$K_D = \frac{[HA]_{org}}{[HA]_{aq}} \qquad \text{Equation (3.3)}$$

Note: the portion of the solute in the aqueous layer that exists as A^- has been ignored.

The distribution ratio

Because solutes are often in solution in more than one form, the **distribution coefficient D,** is a more meaningful term than partition coefficient.

$$D = \frac{[HA]_{org}}{[HA]_{aq} + [A^-]_{aq}}$$ Equation (3.4)

The relationship between D and K_D can be shown from the equilibria involved. In the case of a weak acid the acidity constant, K_a is the equilibrium constant.

$$K_a = \frac{[H^+]_{aq}\ [A^-]_{aq}}{[HA]_{aq}}$$ Equation (3.5)

Which rearranges to:

$$[A^-]_{aq} = \frac{K_a\ [HA]_{aq}}{[H^+]_{aq}}$$ Equation (3.6)

Continued on the next slide

From equation (3.3)

$$[HA]_{org} = K_D[HA]_{aq}$$ Equation (3.7)

Substitution of equations (3.6) and (3.7) into equation (3.4) gives

$$D = \frac{K_D\,[HA]_{aq}}{[HA]_{aq} + K_a[HA]_{aq}/\,[H^+]_{aq}}$$ Equation (3.8)

Dividing the numerator and the denominator of equation (3.7) by $[HA]_{aq}$, gives

$$D = \frac{K_D}{1 + K_a / [H^+]_{aq}}$$ Equation (3.9)

Note: Equation (3.9) includes the $[H^+]$ term, indicating extraction to be pH dependent.

Effect of pH on extractions

Equation (3.8), shown below was developed on the previous slide:

$$D = \frac{K_D}{1 + K_a / [H^+]_{aq}}$$ Equation (3.10)

From this equation, if $[H^+]_{aq} >> K_a$:

- Then D is nearly equal to K_D;
- If K_D is large, the weak acid will be extracted into the organic layer.
- When $[H^+]_{aq}$ is high and thus pH is low, a weak acid will therefore be in the mainly unionised form and as a neutral compound, will readily dissolve in the organic layer and hence be extracted.

Conversely if $[H^+]_{aq} << K_a$ then

$$D = \frac{K_D [H^+]_{aq}}{K_a}$$ Equation (3.11)

Thus in alkaline conditions, a weak acid will be largely ionised, and thus will not be extractable into an organic solvent.

Note: In equation (3.10) there is no term for the concentration of the solute being extracted. This means that the distribution coefficient (extraction efficiency) is **independent** of the initial concentration.

The crucial variable in solvent extraction is the pH. **Anything which affects the pH will affect the extraction efficiency**. For example as the concentration of a weak acid solute increases so will the pH, therefore at higher concentrations, weak acids will be extracted less efficiently. The opposite will be true for weak bases.

The distribution ratio is also independent of the volume ratio of the solvents used for an extraction.

Percentage extracted

D may be independent of the volume ratio of the solvents used, but the **fraction** of solute extracted is not. If a larger volume of organic solvent is used, more solute must dissolve in this layer to maintain the values of K_D and D.

The fraction of solute extracted is equal to the millimoles of solute in the organic layer divided by the total number of millimoles and this is shown in equation (3.12)

$$\%E = \frac{[S]_{org} V_{org}}{[S]_{org} V_{org} + [S]_{aq} V_{aq}} x100$$

Equation (3.12)

Where V_{org} and V_{aq} are volumes of the organic and aqueous phases respectively.

(aside: molarity x cm^3 = millimoles)

Continued on the next slide

$$\%E = \frac{[S]_{org}[V]_{org}}{[S]_{org}[V]_{org} + [S]_{aq}[V]_{aq}} x100$$

Dividing through by V_{org}

$$\%E = \frac{[S]_{org}}{[S]_{org} + [S]_{aq}\frac{V_{aq}}{V_{org}}} x100$$

Dividing through by $[S]_{aq}$

$$\%E = \frac{[S]_{org}/[S]_{aq}}{[S]_{org}/[S]_{aq} + \frac{V_{aq}}{V_{org}}} x100$$

As $K_D = [S]_{org} / [S]_{aq}$ *then*

$$\%E = \frac{K_D}{K_D + \frac{V_{aq}}{V_{org}}} x100 \quad \text{Equation (3.13)}$$

As $$D = \frac{[HA]_{org}}{[HA]_{aq} + [A^-]_{aq}}$$

So when $[A^-]_{aq}$ is small, D approximates to K_D [see equation (3.3)] and can thus replace K_D in equation (3.13)

When $V_{org} = V_{aq}$, then the solute is essentially quantitatively extracted when D = 1000

Multiple extractions

The fraction (F_1) of solute **remaining** in the aqueous phase after one extraction by V_{org} is given by:

$$F_1 = \frac{[S]_{aq} V_{aq}}{[S]_{org} V_{org} + [S]_{aq} V_{aq}}$$

Equation (3.14)

Dividing through by $[S]_{aq}$ gives:

$$F_1 = \frac{V_{aq}}{\frac{[S]_{org} V_{org}}{[S]_{aq}} + V_{aq}}$$

Which, by incorporating equation (3.1), becomes:

$$F_1 = \frac{V_{aq}}{K_D V_{org} + V_{aq}}$$

Equation (3.15)

Continued on the next slide

The fraction (F_2) of solute remaining after a second extraction with a further volume of organic solvent (V_{org}) is given by:

$$F_2 = \frac{V_{aq}}{K_D V_{org} + V_{aq}} F_1 = \left(\frac{V_{aq}}{K_D V_{org} + V_{aq}} \right)^2$$

After 'n' extractions with further volumes (V_{org}) of fresh organic solvent each time, the fraction (F_n) of solute remaining in the aqueous phase will be

$$F_n = \left(\frac{V_{aq}}{K_D V_{org} + V_{aq}} \right)^n \qquad \text{Equation (3.16)}$$

If subscripts '0' and 'n' are taken to denote concentrations initially and after n extractions, the concentration in the aqueous phase after 'n' extractions will be given by:

$$[S]_{aq_n} = \left(\frac{V_{aq}}{K_D V_{org} + V_{aq}} \right)^n [S]_{aq_0} \qquad \text{Equation (3.17)}$$

Using equation (3.17), it is possible to show that a greater extraction efficiency is achieved, by extraction with a number of small volumes of solvent, rather than a single large volume, even though the **total volume** of organic solvent is the same in each case. Example (3.i) below illustrates this difference.

Example 3.i

100 cm^3 of an aqueous solution (0.01M) is extracted into a total volume of 250 cm^3 of ethyl acetate. The distribution coefficient, K_D is 2.30. In the first case, one extraction is performed and equation 14 gives:

$$[S]_{aq_n} = \left(\frac{V_{aq}}{K_D V_{org} + V_{aq}}\right)^n [S]_{aq_0} = \left[\frac{100}{2.3x250 + 100}\right]^1 x0.01 = 1.45x10^{-3} \text{moles remaining}$$

In the second case 5 extractions each of 50 cm^3 are done. Now equation 14 gives:

$$[S]_{aq_n} = \left(\frac{V_{aq}}{K_D V_{org} + V_{aq}}\right)^n [S]_{aq_0} = \left[\frac{100}{2.3x50 + 100}\right]^5 x0.01 = 2x10^{-4} \text{moles remaining}$$

Extraction of metals

One of the main uses of solvent extraction procedures is the removal of metals from aqueous solutions. As metals in aqueous solutions are ionised and organic solvents are used for extraction, the first thought may be that this is not possible.

Therefore, to enable metals to be extracted into organic solvents, they are ‘disguised’ to make them appear organic in nature and therefore readily dissolved in organic solvents. There are three ways of achieving this:

- Ion-association complexes;
- Metal chelates;
- Solvation of ion pairs by organic ligands

Ion association complexes

The simplest of these are ion pairs composed of a large positive and a large negative ion. The tetrabutylammonium cation, $(n\text{-}C_4H_9)_4N^+$ forms extractable ion pairs with a number of anions such as MnO_4^- The resulting ion-pair is not appreciably hydrogen bonded to water and disrupts the strongly hydrogen bonded matrix of the water solvent, so there is a strong tendency for the neutral ion-pair to be 'repelled' into an organic phase.

$$[MnO_4]^-_{aq} + [(n\text{-}C_4H_9)_4N^+]_{aq}Cl^- = [(n\text{-}C_4H_9)_4N^+][MnO_4]^-_{org} + Cl^-_{aq}$$

Ion association complex

Metal chelates

The most widely used method of extracting metal ions, is by forming a metal chelate - reacting the metal with an organic chelating acid.

Most chelating agents are weak acids which ionise in water, the metal displaces the proton when the chelate is formed neutralising the charge on the metal cation. Many metal chelates are highly coloured, which facilitates spectroscopic determination of the metals in the visible region of the electromagnetic spectrum.

The formation of metal chelates is pH sensitive and the same chelating agent will extract different metals at different pH values, depending on the formation coefficient (K_f) of the metal chelate. Therefore it is often necessary to buffer the extraction medium to a suitable pH, in order to quantitatively extract the required metal.

$K_f = [MA_n]/[M^{n+}][A^-]^n$

Some examples of analytically important metal chelates are shown on the next 4 slides.

Ethylene diamine tetraacetic acid

Ethylenediaminetetraacetic acid better known as H_4EDTA or H_4edta, is a commonly used chelating agent as it will chelate with many metals.

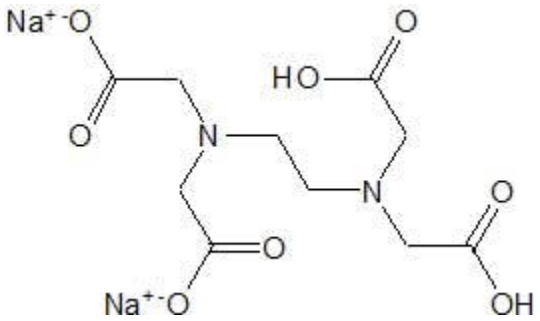


Figure 3.17 - the disodium salt of EDTA

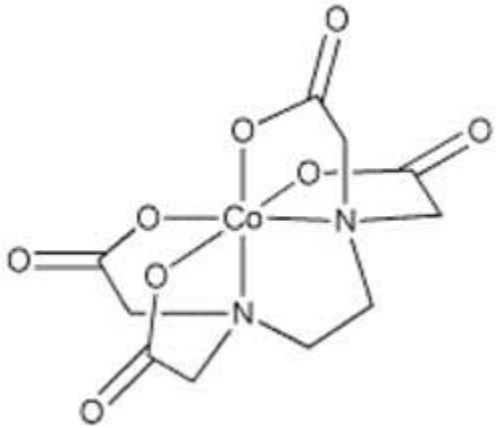
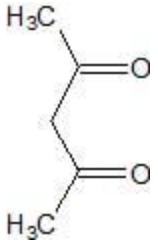


Figure 3.18 - H_2 Co(edta) chelate

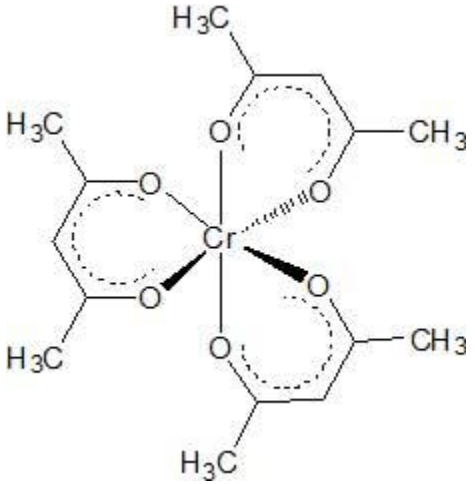
Pentane-2,4-dione (Acetylacetone) and its derivatives

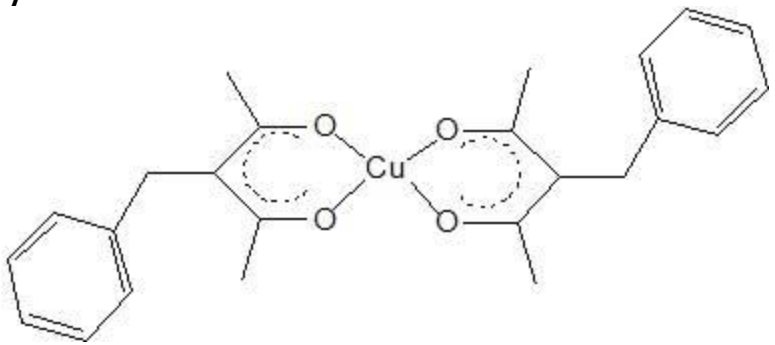
Chelating agents form bonds via electronegative atoms such as oxygen, nitrogen and sulphur. On this slide acetylacetone is shown before and after **complexing** with a metal.



acetylacetone

chromium acetylacetonate

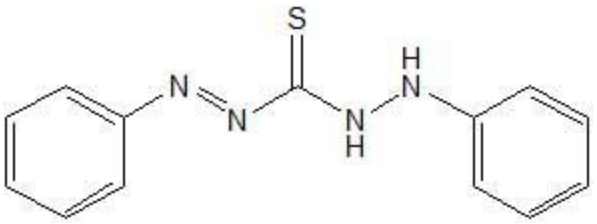




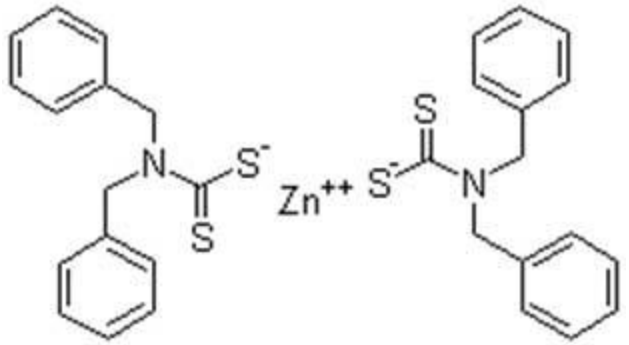
copper benzylacetylacetonate

Figure 3.19 - structural diagrams of acetylacetone and its derivatives

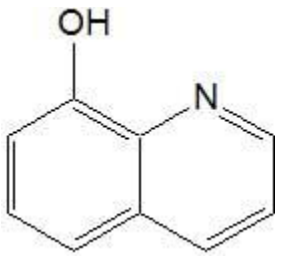
Some examples of other analytically important chelating agent are shown below. Note the presence of sulphur, oxygen and nitrogen which facilitate the formation of bonds with metals.



dithizone



Zinc dibenzyldithiocarbamate – reagent specific for analysis of Cu^{2+}



8-hydroxyquinoline (oxine)

Figure 3.20 - structural diagrams of some other chelating agents

Table (3.4) below gives a selection of chelating agents and the metals with which they complex, at specific pH values.

Ligand	pH	Metal extracted
Acetylacetone (pentane-2,4-dione)	7-8	Be(II)
Dithizone (diphenylthiocarbamazone)	3 5.5 7.3 12	Cu(II) Sn(II) Pb(II) Cd(II)
oxine (8-hydroxyquinoline)	2 – 2.5	Fe(III)

Table 3.4 – examples of extractable metal chalates

Extracting metals as ‘coloured’ complexes, enables the determination of low concentrations of metals; the solvent extraction procedure is followed by spectroscopic measurement (in the visible region of the electromagnetic spectrum) of the absorbance of the solution.

Separations using multiple extractions

Multiple extractions can effectively remove a single species if its D value is different from the other species present. If the D values for two species differ by 1000 only 97% purity of the species with the highest D value can be achieved after a single extraction.

A semi-automated form of solvent extraction, termed countercurrent extraction, can be used to produce extracts of greater purity even when there are only small differences in the D values of the species being separated, however description of this system is outside the scope of this programme.

Figure (3.21) shown on the next slide illustrates how multiple extractions and back extractions may be used to create separations by use of solvent extraction. Assume that:

- Equimolar amounts of solutes A and B are used;
- Equal volumes of both phases are used;
- A single extraction with an organic phase removes 5% of A and 95% of B;
- After each extraction the phases are separated and transferred to the next tube and fresh organic or aqueous phase added

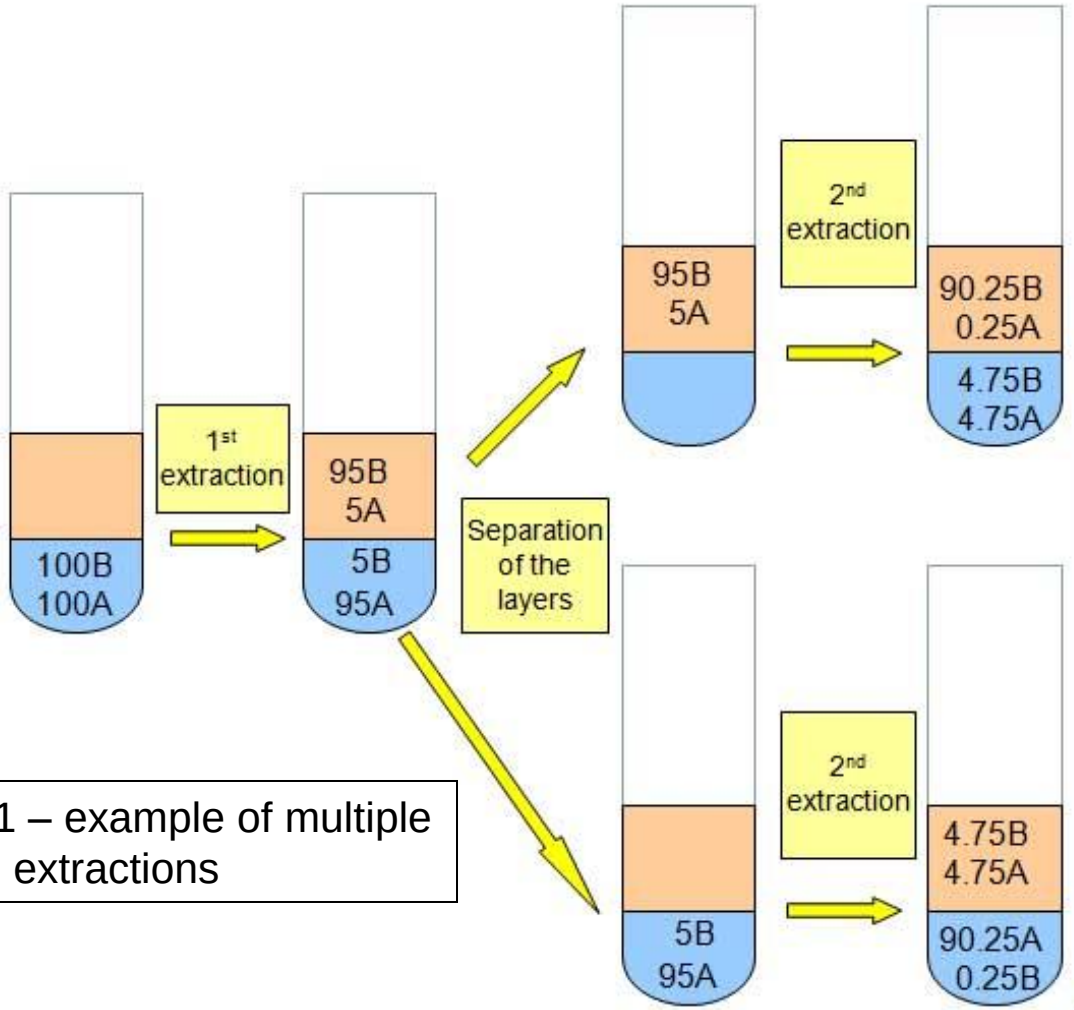


Figure 3.21 – example of multiple extractions

Figure 3.21 illustrates a mixture of 2 solutes at equal concentrations dissolved in water. Following the first extraction, 95% of B is transferred to the phase, whilst 95% of A remains in the aqueous phase. If the two phases are now separated and both re-extracted, the upper organic phase is now composed mainly of component B and the lower aqueous phase, contains mostly component A. Further similar extractions will lead to almost pure samples of both solutes A and B becoming available.

Comments on multiple extraction procedures

The procedure as illustrated in figure (3.21) will eventually be able to produce solutions containing pure samples of both solutes A and B. **However this procedure would be of little use in analytical separations as the two solutes would be separated in a large number of separate portions of solvent**.

The procedure does however have some application in preparative areas of pharmaceutical and natural product chemistry.

Continuous extraction

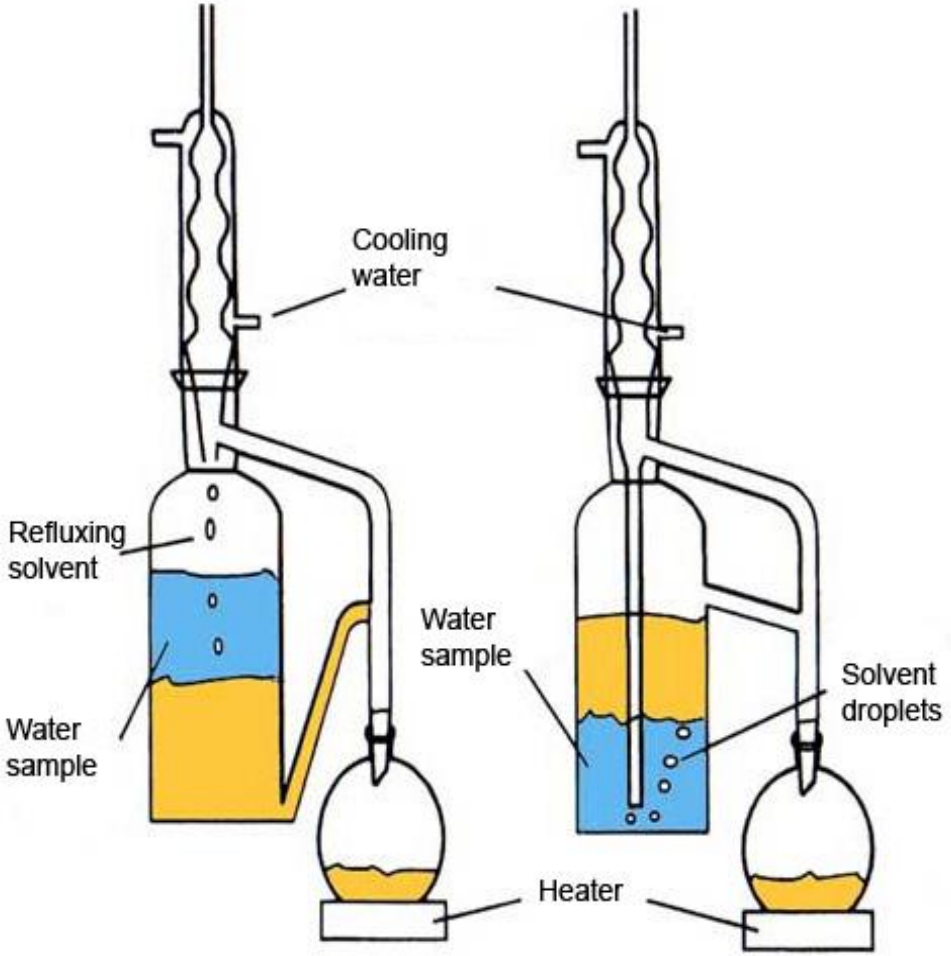


Figure 3.22 - apparatus for continuous extraction

In some instances it is difficult to remove a solute from a sample, unless a very large number of extractions are carried out. In such cases continuous extraction may be preferred as illustrated in figure (3.22)

The apparatus on the **far left** is for continuous extraction with a solvent **more dense** than water. The **right-hand** diagram is apparatus for extraction with a solvent **less dense** than water. Note: Only single solvents can be used in these procedures. Thus These are not suitable for extracting metal chelates.

The advantages of continuous extraction are:

- Only small volumes of solvent are used; (solvent must be single organic species)
- A high percentage of the solute can be extracted;
- The extraction can be left unattended for long periods and can extract from solids as well as liquids.

The solute being collected must be thermally stable under the conditions used and must be less volatile than the extracting solvent.

Figure (3.23) is of a Soxhlet extraction apparatus, suitable for the continuous extraction of solutes from solid matrices. The solid to be extracted is placed in the porous thimble and the solvent in the flask.

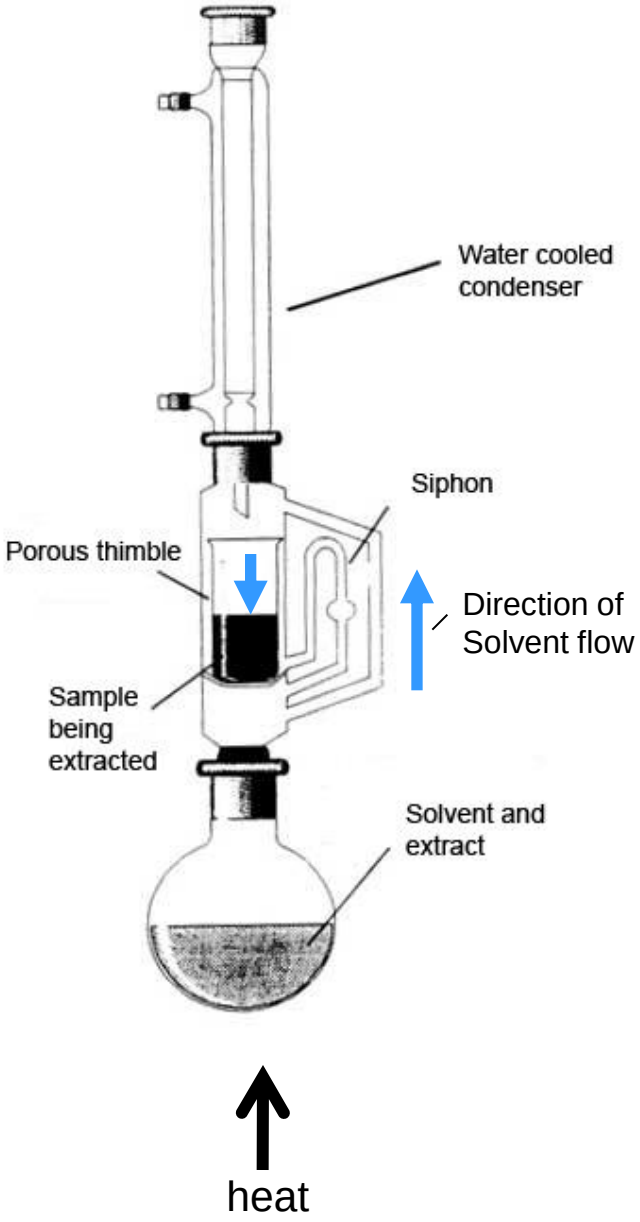


Figure 3.23 – Soxhlet extraction

Accelerated solvent extraction

In accelerated solvent extraction (ASE), the extraction carried out at temperatures above the boiling point of the solvent ie under pressures above atmospheric.

ASE is mainly used to remove soluble solutes from solid matrices, for instance organic constituents from soil and thus represents a modern version of a Soxhlet extraction. It overcomes some of the problems associated with Soxhlet extraction in that:

- Much smaller volumes of solvent used;
- The extractions take less time;
- Extractions are automated
- Multiple samples can be managed.

Figures (3.24 & 25) are photographs of typical ASE equipment

Figure 3.24 – Dionex ASE instrument

Figure 3.25 – extraction cell

Reflection on solvent extraction

Solvent extraction provides a useful method of preparing samples prior to analysis. It is particularly important in removing organic or inorganic constituents from complex matrices such as soil. Many methods have been developed for the measurement of trace metal content based upon the use of metal chelates, however in the 21st century many of these methods have been superseded by the use of atomic spectroscopic techniques.

The disadvantages of traditional solvent extraction are that:

- Large volumes of solvent are sometimes required, although ASE techniques have reduced this considerably;
- Extractions may not be quantitative, however under a given set of experimental conditions, should be reproducible;
- Total separation between two species with differing D values may not be possible to normally accepted analytical accuracy;
- Time consuming process;
- The technique does not lend itself to automation;
- Emulsions can form on shaking which can be difficult to break down;
- Limited to the use of immiscible solvents which historically were chlorinated hydrocarbons.

Question 3.1 Explain why it is necessary to have a sample preparation stage within the analytical process and give two example (one for each) of analytical procedures that both require and do not require, this stage in the analysis to be performed separately. Distinguish between liquid/liquid and Soxhlet solvent extraction processes

Question 3.2 Compare and contrast the techniques of 'Wet digestion' and 'Microwave digestion' as methods for removal of an organic matrix prior to analysis for metallic components in a sample.

Question 3.3 An analyte was dissolved in 50 cm^3 of water to give a 0.2M solution. This solution was shaken with 20 cm^3 of ether. After allowing the solvents to separate analysis showed that there was 1.2 mmol of analyte in the aqueous layer. What is the value of the distribution coefficient, K_D?

Question 3.4 Three 1 cm^3 aliquots of organic solvent were used to extract the analyte in question 1 from a 20 cm^3 aqueous solution of concentration 0.3 M. What was the concentration of analyte remaining in the aqueous layer after the three extractions?

Question 3.5 The distribution coefficient for an extraction is 6.0. Calculate the fraction of solute remaining in the aqueous phase (250 cm^3) after:

- One extraction of 100 cm^3 of an organic solvent:
- One extraction of 20 cm^3 of an organic solvent;
- Five extractions of 20 cm^3 of an organic solvent.

Outline answer to question number 3.1

The answer to this question may be found on slides 4 - 7 and 15 - 18

Although there are analytical techniques that can make measurements directly on the sample taken, this is the exception rather than the norm. Sample preparation is thus required either to remove unwanted components of the sample which would interfere in the measurement process, or to concentrate target analytes such that they can be measured by the equipment available within an individual laboratory, or by the science overall. For instance, very low levels of mercury need to be concentrated on gold, as an amalgam, in order to concentrate the mercury to levels that can be measured by the technologies currently available.

For the analysis of trace metals present in soils or foodstuffs for example, it is necessary to either destroy the substrate holding the target analyte or extract out the analytes from the substrate for subsequent analysis by atomic absorption spectroscopy. Techniques that can require little in the way of sample preparation are, gas-liquid and high performance liquid chromatography, where high efficiency separations are performed as part of the measurement procedure, and X-ray fluorescence spectroscopy, where the fluorescent X-ray emission is separated prior to detection.

Liquid/liquid extraction procedures are used to transfer analytes from one liquid phase to another. For the procedure to be effective, the two liquids chosen should be almost totally immiscible, and the analyte should have a higher propensity for the extracting solvent. Soxhlet extraction procedures are used to remove soluble analytes from insoluble solid substrates. The process is continuous and the extraction can be carried out over a period of many hours.

Outline answer to question number 3.2

The answer to this question may be found on slides 23 - 27

Both techniques are used to destroy organic material, prior to the analysis of inorganic components within the sample matrix. The main generic difference between the two techniques, is that one is open-flask digestion (wet digestion) and the other is the modern closed flask digestion (microwave digestion). It should be noted at this stage that microwave heating has been applied to open-flask digestions, but microwave digestions refer to a closed-flask situation.

Both techniques are capable of using a range of oxidising acids to perform the digestion – nitric, sulphuric and perchloric. However, whereas concentrated nitric acid is only partially successful at performing digestions at atmospheric pressures, it is much more successful at the elevated pressures and temperatures that can be achieved within closed vessels.

By using nitric acid, virtually all metals can be transferred to a solution matrix, whereas sulphuric acid does have a number of sparingly soluble salts, which could precipitate out of solution if the concentrations exceed the solubility product. Also nitric acid is a more acceptable reagent for use with atomic spectroscopic techniques, which will inevitably be used for the final measurement of metal ion content.

Perchloric acid can be used to improve the digestions carried out in open vessels, however because of the explosive nature of this reagent when in contact with some organic matrices it is only recommended for use, following pre-digestion with other acids, and by experienced personnel.

Outline answer to question number 3.3

The answer to this question may be found on slide 41.

> 1.2 mmol of analyte remained in the 50 cm^3 of aqueous solution following extraction into the organic layer.This is equivalent to a solution concentration of 0.024 M

Initial analyte concentration in the aqueous solution was 0.2 M and therefore the total quantity of analyte before the extraction was:

50 x 0.2 = 10 mmol

Thus quantity transferred to the organic solvent was:

10 – 1.2 = 8.8 mmol

This is equivalent to a solution concentration in the 20 cm^3 of organic solvent of:

$$\frac{8.8}{1000} \times \frac{1000}{20} = 0.44 \text{ M}$$

Thus $K_D = [HA]_o / [HA]_{aq} = 0.44 / 0.024 = 18.3$

Outline answer to question number 3.4

The answer to this question may be found on slides 48 - 50

Equation (3.17) needs to be used to solve this problem:

$$[S]_{aq_n} = \left(\frac{V_{aq}}{K_D V_{org} + V_{aq}} \right)^n [S]_{aq_0}$$

Given that:

V_{aq} = 20 cm^3

V_{org} = 1.0 cm^3

K_D = 18.3

$[S]_{aq0}$ = 0.3 M

Putting these values into the above equation gives:

$$[S]_{aq_n} = \left(\frac{20}{18.3x1 + 20} \right)^3 0.3$$

= **0.0427 M**

Outline answer to question number 3.5

The answer to this question may be found on slides 48 - 50

Equation (3.16) needs to be used to solve this problem:

$$F_n = \left(\frac{V_{aq}}{K_D V_{org} + V_{aq}} \right)^n$$

Where F_n relates to the fraction of solute remaining after 'n' extractions have been carried out, and other algebraic terms are as used in the previous question

Answer to (a): $F_1 = 250/[(6 \times 100) + 250] =$ **0.294**

Answer to (b): $F_1 = 250/[(6 \times 20) + 250] =$ **0.675**

Answer to (c): $F_5 = 250/[(6 \times 20) + 250]^5 =$ **0.141**

From these results we can see that a number of extractions using a small volume of solvent (part c) is a more efficient process than performing one extraction with the same total volume of solvent (part a).