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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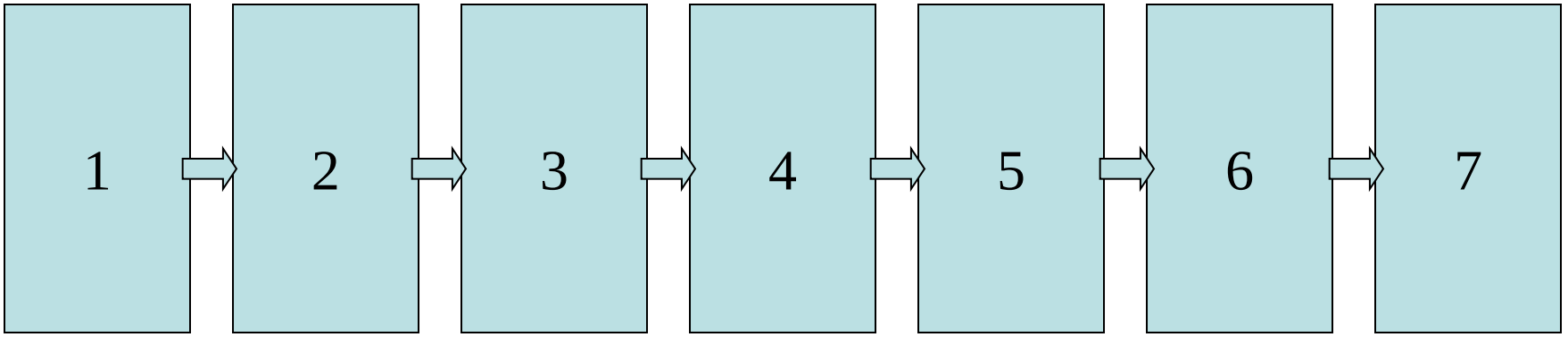
Chapter 2: ‘Analytical Process’ unit 3 - Sampling

Contents

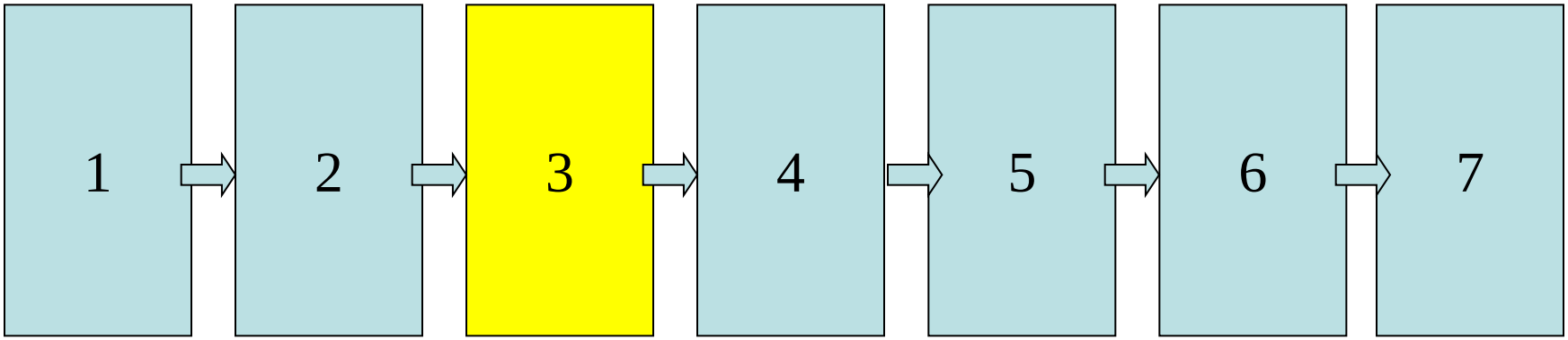
The analytical process model – revision slide

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 3 – sampling



Sampling is the most important stage in the analytical process and is the stage likely to produce the highest proportion of the total error ('uncertainty') in any analysis. Great care therefore needs to be exercised when taking samples, in order to minimise this error component. A sample should be '**representative**' of the bulk from which it was removed, and once taken, should be stored in such a way such that it retains it's '**integrity**' (not alter it's structure or lose components) prior to the analysis being carried out.

*** see 'Glossary of Terms'**

Introduction

Because of the ever increasing number of analyses required, combined with the increasing complexity of the samples to be analysed and the need for rapid (if not instant) results, new sciences, technologies and methodologies are continually being developed. Except in a few instances, current instrumentation has not as yet evolved to the point where it is possible to take an analytical instrument to an object or material to be analysed and for all of the required information to be obtained [*eg: a tricorder in Star Trek*].

Most analytical measurements are thus still made by removing a portion or part of the material to be analysed [termed the **sample**] and taking it to a laboratory for analysis. Analytical measurements are thus being made not on the material itself, but on the **sample** portion that has been taken from the material to be analysed

It is essential therefore, that if the results of the analysis are to be meaningful, the utmost care must be taken when selecting the sample for analysis.

The act of sampling would pose very few problems if all materials etc. that were to be sampled were known to be, or could be considered to be, **homogeneous**. Unfortunately in the 'real world' this is rarely the case. **Homogeneous** in this instance refers to both the constitution of the material to be sampled (components and substances that are present) and the state in which they exist (particle size for instance). Gases and liquids are often considered to be homogeneous, but this assumption is only likely to be valid when small fixed quantities of these are to be sampled.

Example: a 1l bottle of a single-phase liquid may be shaken thoroughly to ensure homogeneity and from then on, even the smallest sample taken from the bottle will constitute a **representative sample**.

Solid matrices (eg: tablets, soils, minerals etc.) should normally be considered as **heterogeneous**, although the extent of heterogeneity may vary considerably. The more **heterogeneous** the matrix the larger the sample size needed to constitute a **representative sample**

Definition of a representative sample

A portion of a material taken from a consignment and selected in such a way that it possesses the essential characteristics of the bulk

It is essential that once the sample has been taken, the **integrity** of that sample is then maintained through to analysis

Definition of integrity

Integrity in this context, refers to the structure and composition of the sample being the same when analysed as when it was taken

Example: losses of volatile components or oxidation of metallic components to higher valence states would constitute a loss of sample integrity, thereby invalidating the analysis due to loss of sample representation. It is therefore Imperative that care is taken with the storage of samples, so that sample integrity is maintained.

As will become evident later, particularly with samples of solid matrices, once the initial sample has been taken, there are likely to be a number of additional sub-sampling stages prior to analysis being carried out. **It is imperative that at each of these additional stages, sample representation is maintained such that the portion of the material eventually analysed still remains representative of the bulk of the material from which it was originally taken.**

Sampling introduction – reflection

- Most analysis are carried out on **sample** portions of the material that requires analysis
- Most matrices should be considered at **heterogeneous** rather than **homogeneous**
- The greater the extent of heterogeneity, the larger the sample size required
- Sample must be taken so that they are **representative** of the material being sampled
- Samples must be stored appropriately so that sample **integrity** is maintained

Generic sampling procedures

A **sampling procedure** may involve many steps before the analysis for the target analytes is carried out. It cannot be over-emphasised that as the size of the analytical sample maybe only a gram or so and that this in turn may relate to many tonnes of original material, great care must be exercised at all procedural stages to ensure that representation is maintained

Definition of 'Sampling procedure'

The succession of steps set out in a specification, which ensures that the sample eventually taken for analysis shall possess the essential characteristics of the bulk

There are many terms that are regularly used in sampling terminology. These are:

- Consignment
- Sampling unit
- Increment
- Composite/aggregate/gross sample
- Sub-sample
- Laboratory sample
- Test Sample
- Samples for analysis

The relationship between these terms is shown on the next slide

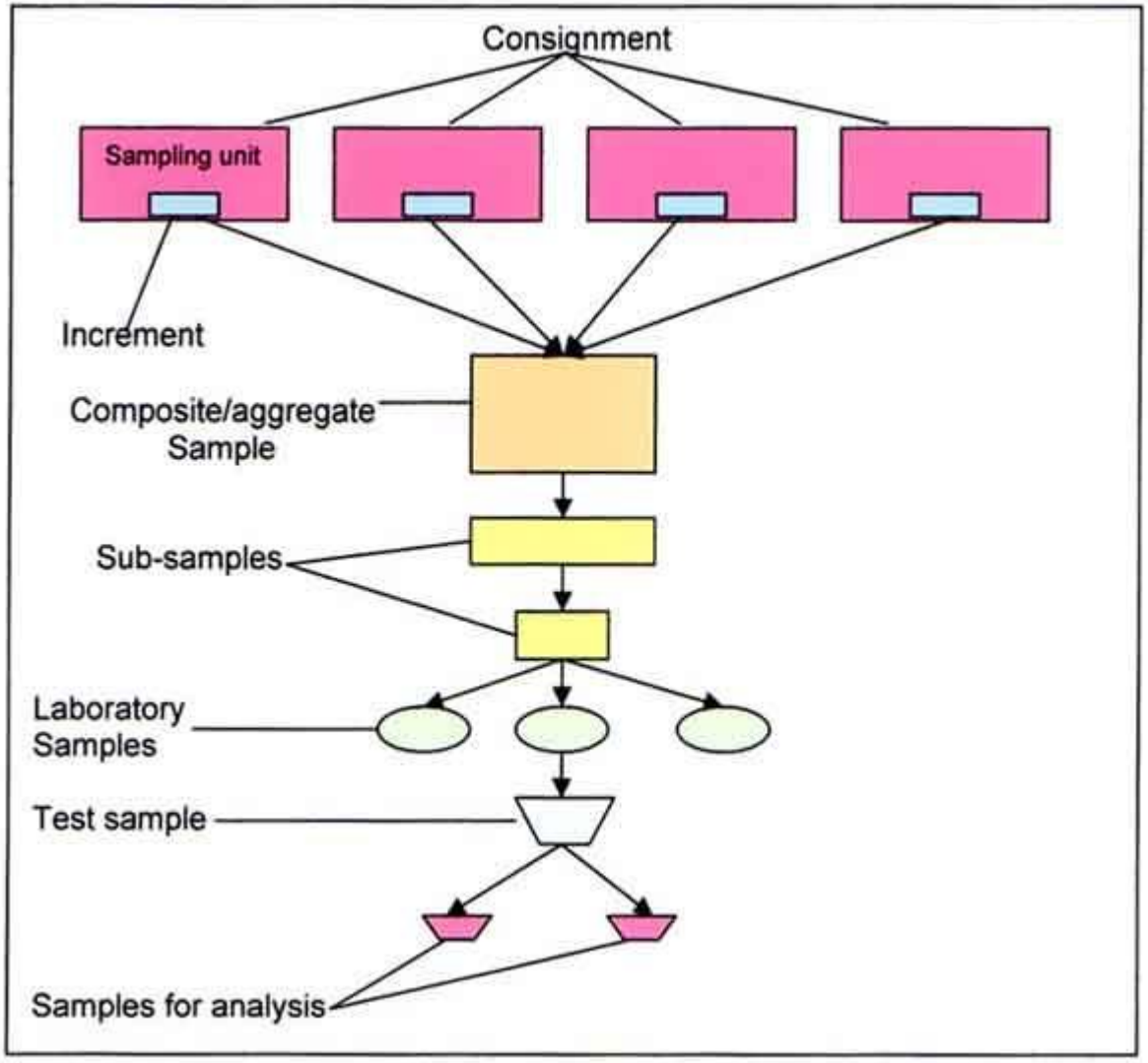


Figure 2.0 relationship between sampling terms

A **consignment** may consist of a number of **sampling units.** An **increment** is that portion removed from the **sampling unit**. The **increments** may be analysed separately, but more likely be combined to produce a **composite** sample. This **composite** sample will generally be too large and will thus need to be sub-sampled before transfer to the laboratory for analysis. The **laboratory** sample is in turn sub-sampled to produce a **test sample** and **samples for analysis.** Where **sampling units** are very large, it may be necessary to take more than one **increment** from each unit

Note: definitions of all terms in bold blue may be found in the 'Glossary of Terms'

Design of a sampling plan

Definition of a Sampling Plan

A predetermined procedure for the selection, withdrawal, preservation, transportation and preparation of samples taken for analysis

The design of a **sampling plan**, is the logical next step following identification of the objectives for carrying out the analysis and decision on the analytical procedures to be adopted. Devising a **sampling plan** requires five further decisions to be made:

- Identify sampling locations
- Decide on the number of increments to be taken and the methods by which they will be taken
- Select suitable sub-sampling routines in order to produce the laboratory sample
- Select methods for sample preservation, storage and transport
- Be prepared to review the plan in the light of experience and experimentation

The sampling plan will need to take into account, the reasons for the analysis and particularly how accurate the final analytical measurement needs to be. An analytical measurement with wide specification limits require a less accurate and careful sampling procedure than one with narrow specification limits.

Identify sampling locations

This is one of the most difficult decisions to be made when devising a sampling plan Although relevant literature (Analytical journals for instance) will be able to provide some guidance, common sense will also prove useful, as will an understanding of statistics.

Example: Consider a warehouse containing a **consignment** of separate pallets, each pallet containing 64 boxes (**sampling units**) of tinned meat imported from outside the European Union. The consignment needs to be monitored for particular bacteria, growth promoters and heavy metals. The decision has to be made as to **which boxes are to sampled and then which tins inside each box are to be sampled**. Common sense denotes that it would be wrong to choose all of the tins to be analysed from those boxes which were the easiest to reach as this introduces individual **bias** into the decision making process. To eliminate possible **bias**, all of the boxes must have **an equal chance of being sampled**. Thus the boxes should all be mentally or physically numbered and then selected by using a set of random number tables. Once the boxes have been selected, a similar process can be used to select individual cans for analysis.

Increments

Having identified the sampling location(s) the following decisions need to be made:

- How many **increments** to take from each sampling unit;
- How will these be taken.

The number of **increments** will depend upon:

- The overall size of the **consignment** – the larger the **consignment** the greater the number of **increments** required.
- How heterogeneous the **consignment** is considered to be – the greater the heterogeneity, the greater the number of **increments**.
- The accuracy required for the final analytical measurement – the larger the measurement uncertainty to be allowed, the smaller the number of **increments** and vice-versa.

Remember that **increments** can be combined together (to produce a **composite** sample) or analysed separately. **Separate analysis will produce a more accurate answer, but can be considerably more expensive**.

Sampling methods

This term refers to both the tools to be used to collect the samples and the sampling situation – is the system to be sampled static or dynamic (in motion)?

Example of a dynamic sampling situation

Figure (2.1)

Consider for instance a grain silo, where the grain inside the silo needs to be analysed for traces of pesticides. Figure (2.1) shows a typical grain silo, effectively a sealed unit, which would be extremely difficult to sample. The preferred sampling plan would therefore be to take samples of the grain whilst it is being transferred to trucks, lorries etc. This would relate to a **product in motion**, and samples (**increments**) would be taken at fixed time intervals dependent upon the number of samples considered necessary to produce an outcome of acceptable accuracy. The number of increments to be selected would depend upon past experience, or from results obtained during the development stage of the sampling programme.

Sampling methods for static sampling situations

Sampling methods for static sampling, generally refer to the tools that are used to collect samples. Specialist tools are available to enable samples to be taken from a variety of possible matrices. Considering solid matrices for example there are:

- Scoops for sampling general heaps;
- Devices for cross sectional sampling from drums of powder or tablets;
- Grab type sampler for sampling river, lake and sea beds;
- Spears for depth sampling from grain stores.

Similarly, there are range of sampling tools designed for liquid matrices, for example

- Depth samplers for sampling of liquids in drums;
- Weighted bottles for depth sampling of deep water courses.

In highlighting specialist sampling equipment, it is important not to forget the possible use of simple clean glass apparatus (beakers, bottles etc.), spatulas, spades and shovels etc. when appropriate. **Diagrams and photographs to illustrate some of these are shown on the next five slides**

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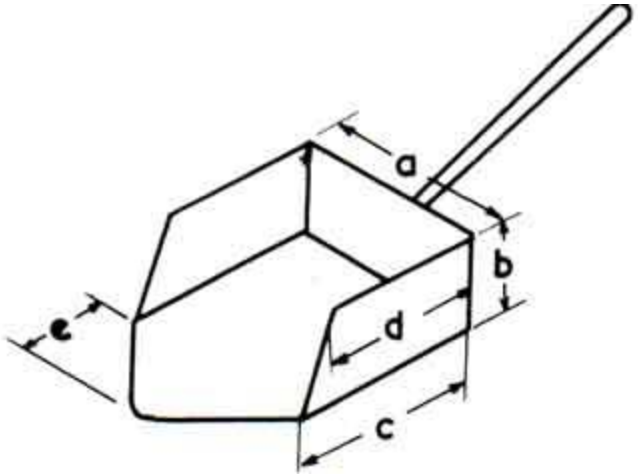

Fig 2.2 – sampling scoop for solid materials

Figure (2.2) shows a typical sampling scoop with high sides, to prevent any of the sample taken, from being lost during transference. The letters [a – e], refer to dimensions recommended for specific sampling purposes. In general, the smaller the average particle size, the smaller the overall capacity of the scoop.

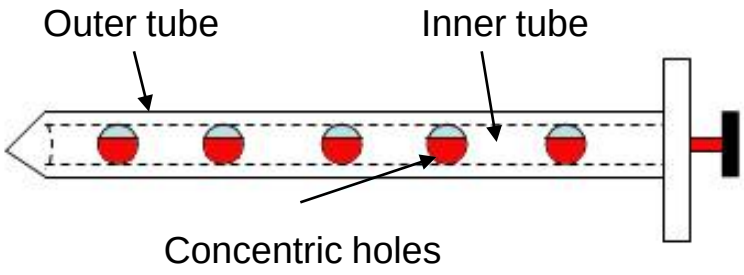

Fig 2.3 – cross sectional sampler for sampling of powders and small particles

The device shown in Figure (2.3) consists of two tubes, one sitting tightly inside the other. The tube is pointed to aid insertion into the unit to be sampled, and both tubes have holes at corresponding positions. The device is inserted with the inner holes closed. When a suitable sampling position has been reached, the inner tube [shown in red] is rotated to open the inner set of holes. The grains, powder etc. then enter the inner tube. The holes are then closed again and the sample withdrawn.

Fig 2.4 – spear device for vertical sampling of grains

In the sampling device shown in Figure (2.4), the spear is forced into the mound of grain to be sampled, with the sampling slot shown, covered by the outer tube. On attempting to remove the spear the cover is displaced and the grain then enters the hollow sampling tube. This device thus allows for samples to be taken from a range of depths from the grain store.

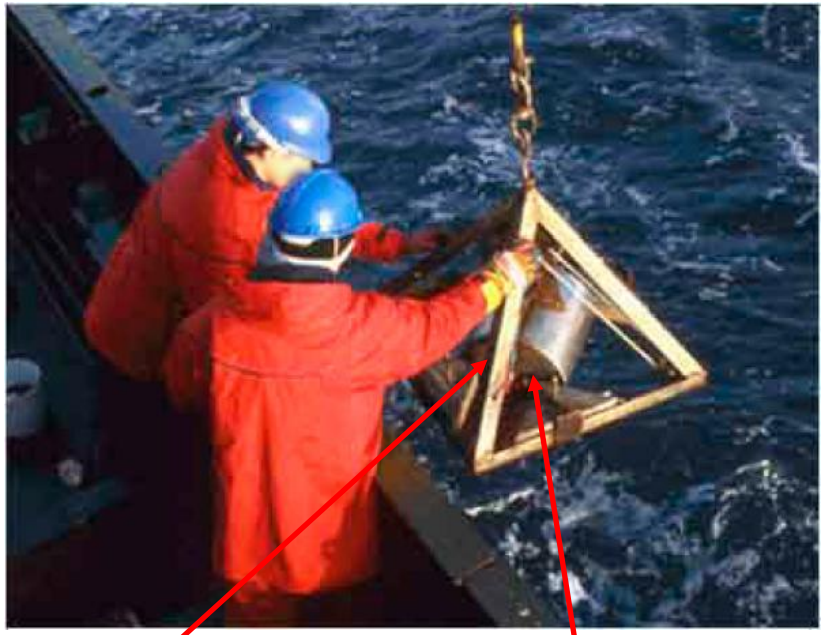

Fig 2.5 – grab sampler for sampling ocean beds

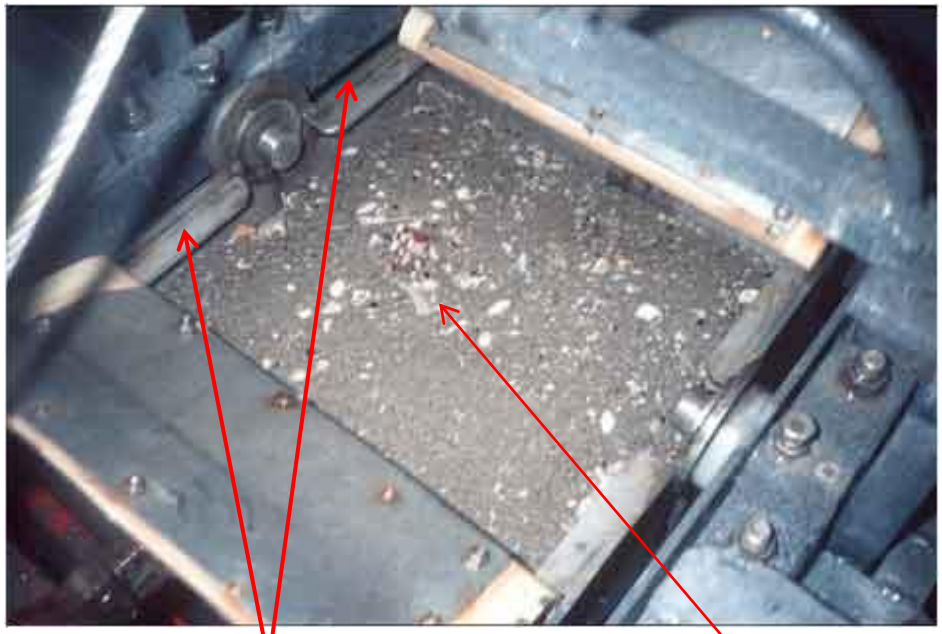

Fig 2.6 – sample of ocean bed captured by the grab sampler

Figures (2.5) & (2.6) show a device used to take sediment samples from a sea bed. The device is lowered into the sea using a winch. The semi-circular metal jaws shown In figure (2.5) are in the open position. They are securely locked together when the device is lowered into the water. Attached to them is a secure but flexible cord. When the metal frame has settled on the sea bed, the line is held taut and a lead weight dropped down on the line. When the lead weight hits the metal frame, it causes the jaws to snap shut. Given the semi-circular design of these jaws, it is able to capture a sample of the sediment. The whole is then hauled to the surface, for the sample to be removed dried and separated.

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The sampling device shown in Figure (2.7) consists of a thick walled glass bottle securely held inside a heavy lead container.
The container is lowered into the water course to a suitable depth as measured by the calibrated rope (shown in red). The stopper is now opened remotely using the blue rope, allowing water to fill the glass bottle from that depth The spring loading at the top of the device allows the stopper to be replaced once sufficient time has been given for the bottle to fill. The container is then hauled back to the surface.
The water sample is now available for analysis.

Figure 2.7 – typical bottle used for depth sampling

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Fig 2.8 – drums containing waste chemicals

Figure (2.8) shows some drums containing a mixture of waste chemicals. Given that the cost and nature of disposal will depend upon the substances stored in the drums, it will be necessary to take samples from varying depths in order to gain an accurate picture of what is stored.

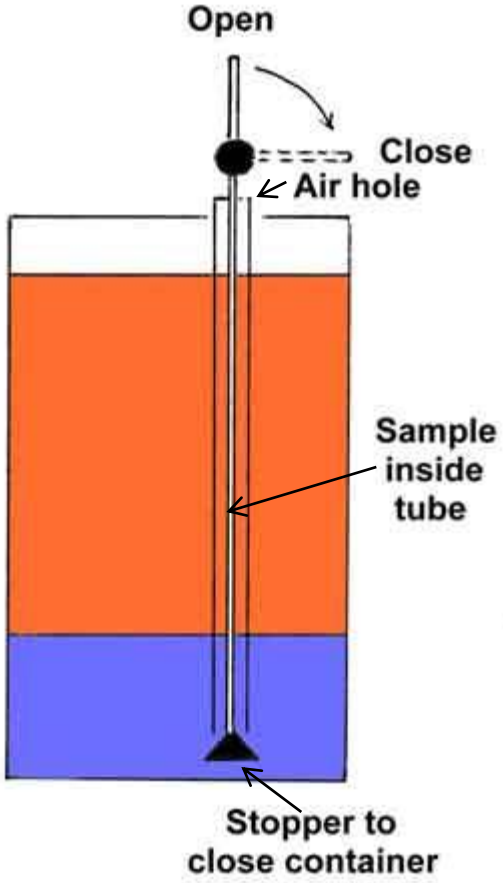

Fig 2.9 – open tube sampler

In the sampling device shown schematically in figure (2.9), the device in the open position is lowered carefully into the tank of liquid to be sampled. The air hole at the top of the device allows a through 'cut' of the liquids inside the tank to be taken as a sample. The handle at the top of the device is now moved to the closed position which draws up the stopper to seal the liquid sample inside the tube. This can now be withdrawn. In this illustration the tank is shown to have two immiscible liquids represented by the two different colours.

Sub-sampling routines

Definition of sub-sampling

Reduction in the size of samples or composite samples whilst retaining sample representation

Figure (1.6), [shown on slide 9], is a schematic representation of a typical sampling protocol. The **composite** sample accumulated by combination of a number of individual sample **increments**, may well be too large to send to the laboratory for analysis and thus **sub-sampling** will need to take place. Further **sub-sampling** may also need to be carried out within the laboratory to produce a test portion for analysis. In both of these situations, similar techniques and procedures are likely to be used, although the sizes of the individual pieces of equipment chosen to be used are of course going to be different. **It must be recognised that the more times that sub-sampling occurs, the higher the uncertainty (margin of error) in the final analysis data.**

There are two methods popularly used to sub-sample solid materials:

- Coning and quartering;
- Riffling.

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Samples may require particle size reduction (**comminution**) prior to sub-sampling. A range of equipment is available for this purpose. Fig 2.10 shows a laboratory version of a typical ball mill. Larger versions of this type of equipment are also available to handle larger quantities of materials.

Definition of 'Comminution'

The general term used to describe processes for particle size reduction and includes crushing, grinding, pulverising etc.

A B C

D

Fig 2.10 – planetary ball mill and containers

Sample is placed in the container (A) with suitable sized balls (agate in this example). The lid is then placed on the container (B) and held tight with the plastic cap (C). The container is then placed in the ball mill and clamped in place (D). Lid is then closed and clamped shut. The mill is then subjected to vibration, rotation, shaking etc to facilitate crushing and grinding of the sample.

Coning and quartering

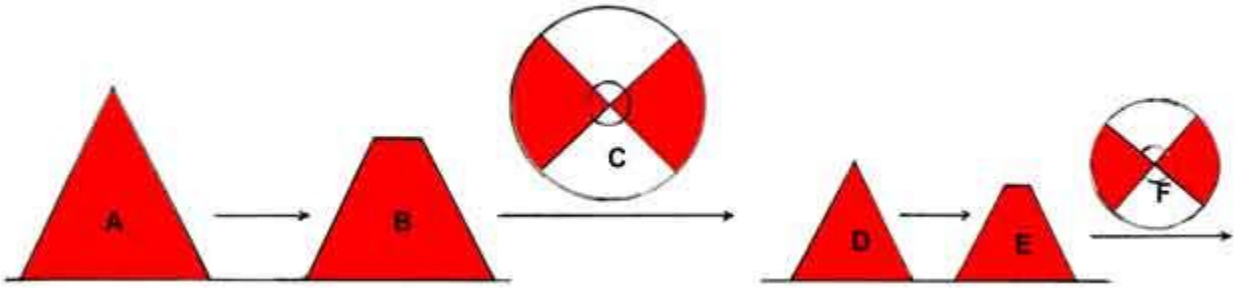

Fig 2.11 – schematic representation of coning and quartering

The material to be sub-sampled is placed on a clean flat surface and by using a shovel or other suitable tool (dependent upon the quantity to be sub-sampled), the material is formed into the shape of a cone [A]. It is particularly important to use **all** of the material and that any fine particles remaining must be spread over the top of the cone. The cone is then flattened at the top and divided approximately into four equal quarters [B & C where C is a birds eye view of the flattened cone]. An opposite pair of quarters is chosen either as the sample, or to form another cone, for the process to be repeated [D, E & F]. The process is repeated until a sample of suitable size to send to the laboratory, is obtained. It may be necessary to reduce the average particle size by crushing, prior to forming cone (A). The size of sample normally sent to the laboratory for analysis will be between 100 g – 1 kg and this may in turn be sub-sampled within the laboratory to produce test portions for analysis.

Riffling

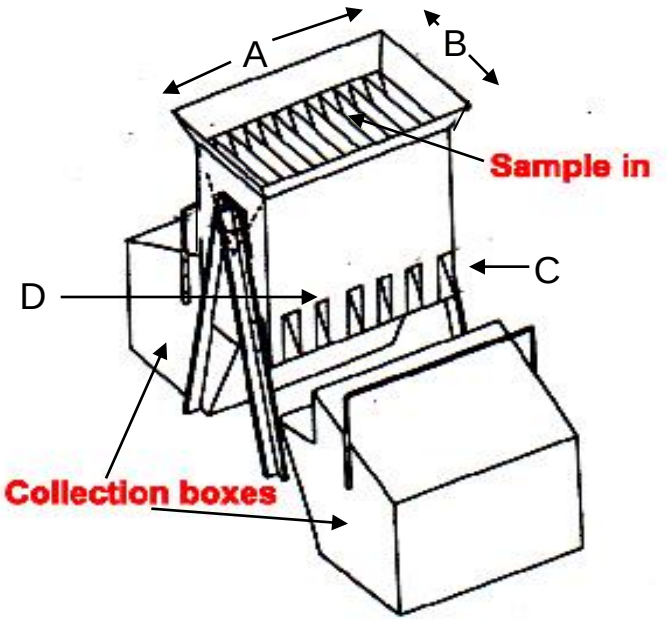

Fig 2.12 – schematic diagram of a typical riffler

The letters 'A', 'B', 'C' & 'D' refer to dimensions for particular applications. Increased accuracy of sub-sampling is obtained, as the distance between the plates is decreased

The material to be **sub-sampled** is crushed such that the dimensions of all particles in the sample are considerably less than the distances between individual plates in the Riffler. The sample is poured evenly across the sample inlet and then emerges on opposite sides in two approximately even portions. The sample collected in one of the boxes can then be **sub-sampled** again if required.

Fig 2.13 shows a small riffler suitable for laboratory use.

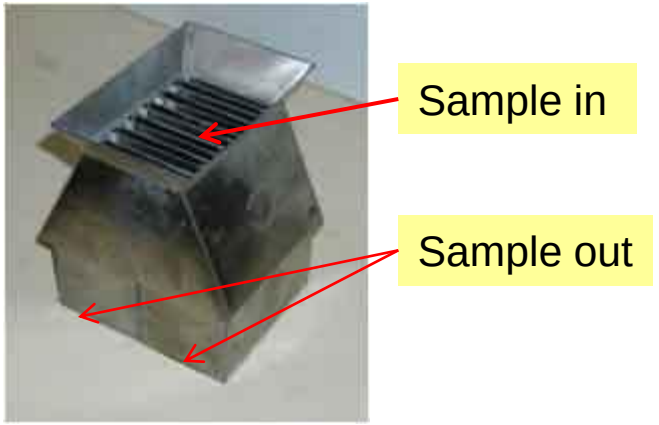

Fig 2.13 – laboratory riffler

Sub-sampling of liquids

No special equipment is required to sub-sample liquids, just common sense!

Liquids that appear by sight to be homogeneous, can be shaken and then a sub-sample transferred to a clean glass or plastic bottle.

Liquid samples that contain an obvious sediment should preferable be filtered and then treated as separate solid and liquid components. This process, although simple in a laboratory, could prove difficult in a 'field' situation. Sample may need to be homogenised using shaking/stirring etc. and then sub-sampled immediately, before the sediment is allowed to settle.

Liquid samples showing two distinct immiscible layers, are best treated as two different samples. Before the sub-samples are removed however, it is important to measure the relative volumes of the two layers. With this type of sample, it is preferable for the whole of the sample to be sent to the laboratory, as they are likely to be a in a better position to carry out representative sub-sampling.

Sample preservation - storage & transport

It is vital to ensure that sample **integrity** is maintained between the time when the sample was taken and when it is analysed. Many types of sample can be affected by storage under inappropriate conditions. This is particularly the case with samples of a biological nature, where components of the samples (eg enzymes), can cause sample change almost as soon as the sample has been taken. Other changes that can occur include:

- Loss of volatiles – (eg: from a soil sample contaminated with hydrocarbons);
- Change in speciation of the analyte – (eg: oxidation state);
- Loss of trace metal ions due to adsorption onto the walls of the sample container;
- Condensate from air or gas sample.

To avoid losses/changes, samples must be stored in containers appropriate to the analyte and held at temperatures sufficient to maintain sample stability.

- Use darkened glass or plastic bottles and jars, where exposure to light can affect changes to the sample;
- Store at below ambient temperatures to reduce the rate of chemical reaction and biological activity. [Refrigeration @ 4^0C or freezing @ -20^0C]

Sample containers

Glass and plastic containers are both used.

Glass containers

- May be clear or opaque with airtight lids – avoid rubber sealing rings or plastic inserts. Easy to clean and are thus re-usable.
- Glass usually considered as inert, however sodium, silicon & boron can all leach from borosilicate glass

Plastic bottles

- Polyethylene or polypropylene (more rigid) are normally used – avoid rubber sealing rings
- Plastic bottles may be more difficult to clean and are thus often discarded after use.
- Polyethylene bottles normally contain plasticisers that can leach into the sample. They can also contain traces of catalysts which can contaminate acid solutions stored for trace metal analysis.
- Plastic bottles are recommended for samples that are to be frozen

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Sampling plans - reflection

- A sampling plan is an empirical set of steps to ensure that a representative sample is presented for analysis
- It is important to pick the most appropriate sampling locations so as to avoid individual bias
- The number of increments required will depend upon the size of the consignment being sampled, the apparent homogeneity of the consignment and the level of uncertainty allowable for the final result.
- Increments may each be analysed separately or composited together. Analysis using composited samples will generally be less expensive overall but may be less accurate in identifying variability of the matrix.
- Samples can be taken from the consignment using appropriate readily available tools, or in some cases by using specially designed sampling apparatus
- Samples may sometimes best be taken from a dynamic (in motion) rather than a static situation
- Samples may need to be reduced in size before submitting for analysis. This process of sub-sampling needs to be designed to retain sample representation
- Important to retain sample integrity during preservation, storage & transport

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Sampling of solid materials

Unfortunately there is no single generic procedure that can describe the sampling of all solid matrices. Solid matrices that require sampling include:

- Sampling from large heaps – consignments transported by ship, railway wagons, lorries;
- Sampling of grains and other free-flowing solids – cereals, powders;
- Sampling from bales – cotton fibres, hay, silage etc.;
- Sampling of metals and alloys – extruded metals and ingots etc.
- Sampling of separately packaged items – boxes, cans, sacks etc.;
- Sampling of soils and sediments;
- Sampling of pharmaceutical products – tablets, powders, emulsions & liquids;
- Sampling of foodstuffs.

Each of these sampling situations poses a unique problem. From research and experimentation, sampling protocols and specific pieces of equipment have been designed, that can facilitate the taking of representative samples and thereby provide reliable analytical data.

The next few slides show examples of sampling procedures for some of these situations

Sample variability

The two diagrams Figures (2.14) & (2.15) show two extremes of sample variability

Fig 2.14

Figure (2.14) shows a grab sample of sediment from an area of the North Sea. The variability of the sample is evident, the sample containing stones and pieces of shell in addition to the sediment.

Given that the objective of the analysis is the composition of the sediment, it is necessary to separate out the unwanted elements of the sample, prior to drying and sub-sampling of the sediment component.

Fig 2.15

Figure (2.15) shows a sample of a finely ground soil, sold commercially as a certified reference material (CRM).

Although this product will show very little variability, it cannot strictly be described as 'homogeneous'. When used as a CRM, the suppliers will recommend the minimum weight to be taken in order to overcome any heterogeneity and to guarantee the accuracy of the material as an analytical standard.

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Soil sampling

Soils are sampled for agricultural (texture and mineral composition for instance) or for environmental purposes (presence of pollutants). The tools used for the sampling of soils are usually very basic – spades and trowels etc., although core sampling devices are available when depth profiling is required. Samples of soil are taken at depths appropriate to the information required. For instance, when sampling a soil to assess nutrients available to a deep-rooted plant or tree, the sample must be taken from such a depth and position appropriate to the root growth. Similarly for shallow rooted plants, a depth of sampling not exceeding 200 mm might be appropriate.

Figure (2.16) shows a spade being used to sample a soil to a depth of about 200 mm. The red outline shows the approximate perimeter from which the soil sample was taken.

Fig 2.16 – soil sampling

Fig 2.17 – soil sample

The soil sample taken in Figure (2.16) is transferred to a clean contamination free surface and allowed to air dry [Figure (2.17)

Soil samples where possible are air dried, provided that the analytes are not volatile.

[Note: Samples taken for the analysis of volatile constituents such as hydrocarbons and other volatile organic compounds must be stored wet in a sealed container, generally at temperatures below ambient.]

Once the sample has been dried, the twigs and stones etc. will be removed by hand, prior to comminution and sub-sampling. Comminution can be achieved in this instance by grinding in a mortar followed by sieving.

These processes are shown on the next slide

Fig 2.18 – grinding and sieving a dried sample of soil

Figure (2.18) shows the dried sample being ground in a mortar to produce a roughly ground material This is then transferred to a 2 mm sieve and the sample not passing through the sieve is then further ground until all of the sample is below the 2 mm threshold.

The final ground sample as shown in Figure (2.18) should be acceptably homogeneous and can now be transferred to a clean and dry storage container to await analysis. No further sub-sampling should be required, however it is advisable to mix the dry sample just before the analysis sample is taken as the very fine particles tend to settle at the bottom of a container during storage

Depth profiling of soils can be achieved by using corers or augers Figure 2.19 shows images to illustrate their usage.

Fig 2.19 – corer sampler being used to sample peat

The tube sampler as shown in Figure (2.19) is screwed, by using the handle at the top, into the ground. It cuts a wedge of soil that remains within the hollow tube. On removal, the device is laid on a flat surface and the top half tube removed or opened to reveal the sample. The sample may then be divided into a number of separate individual samples identified by the depth from which they were taken.

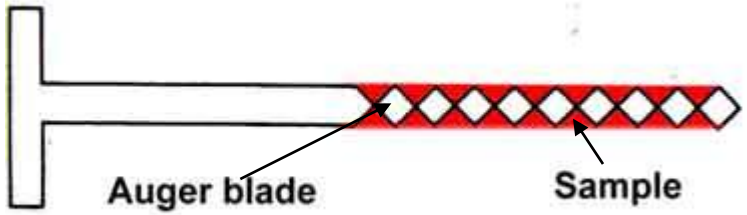


Fig 2.20 – auger sampler

The auger illustrated in Figure (2.20) is screwed into the compacted soil to the depth of the blade. On removing the device, by pulling straight out of the soil, the compacted soil remains attached to the blade as shown in red on the diagram and can be removed for analysis

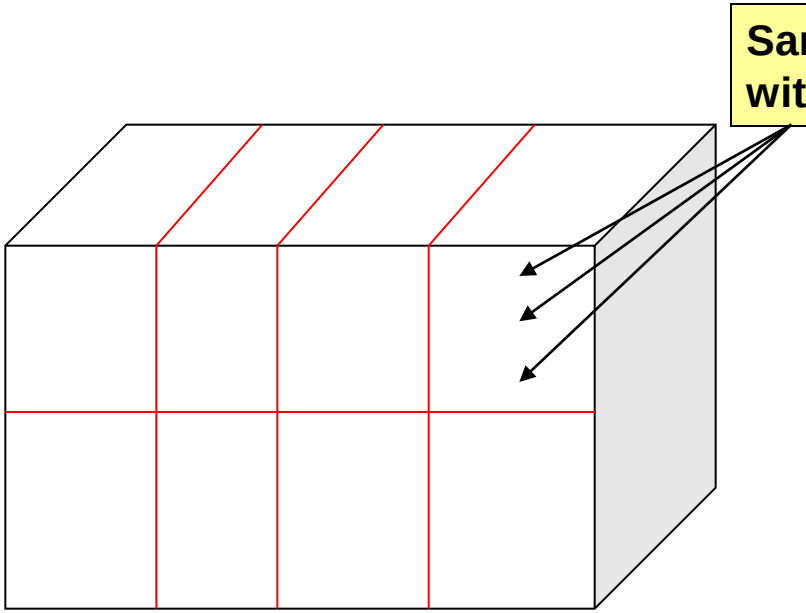
Sampling from large heaps

Large heaps refers to the situations when lorries, and railway wagons transfer their consignments to single piles and to the sampling of individual consignments being transported by boats, lorries and railway wagons. Unfortunately, when particles differ in size or density, then segregation will occur, resulting in the smaller particles having a greater abundance at the base of the heap. This poses a problem for the sampler attempting to take a **representative sample**, in that the basic premise in representative sampling, "**that all particles must have an equal chance of being taken**", is difficult to achieve. When using a sampling scoop to take the sample, the size of the scoop must be such as to accept even the largest of the particle (lump) sizes.

Fortunately in many instances where sampling and subsequent analysis is required, the allowable measurement uncertainty will be large so that the process of sampling can be less accurate. However in the case of natural minerals for metal extraction, where the price paid for the mineral is dependent on the average metal content, then an error in the sampling could be costly to the buyer.

A possible way of tackling this problem is by the process of **Imaginary sectioning**. [see next slide]

Imaginary sectioning



In this concept, the container is mentally divided into a number of imaginary sections [8 in Fig (2.21)] and samples (increments) removed from the top, middle and bottom of each section. These increments will then be composited and sub-sampled as described earlier. However this process is easier said than done!

Fig 2.21 – container divided into sections

A process based upon this concept may be used for the sampling of small static heaps (< 1 tonne), where no other alternative exists. The heap is divided imaginatively into a number of small heaps and increments taken from the top, middle and base of the pile and composited together to produce the gross or aggregate sample. For high variability heaps, the incremental size will need to be about 1 kg, whilst for low variability heaps, 100 g increments will probably be adequate.

Sampling of solid materials in motion (dynamic sampling)

Because of the difficulties with utilising the concept of imaginary sectioning the sample obtained at the end will never be truly representative. The most satisfactory manner in which these types of materials can be sampled, is during the loading or unloading operation, preferably via a conveyor belt.

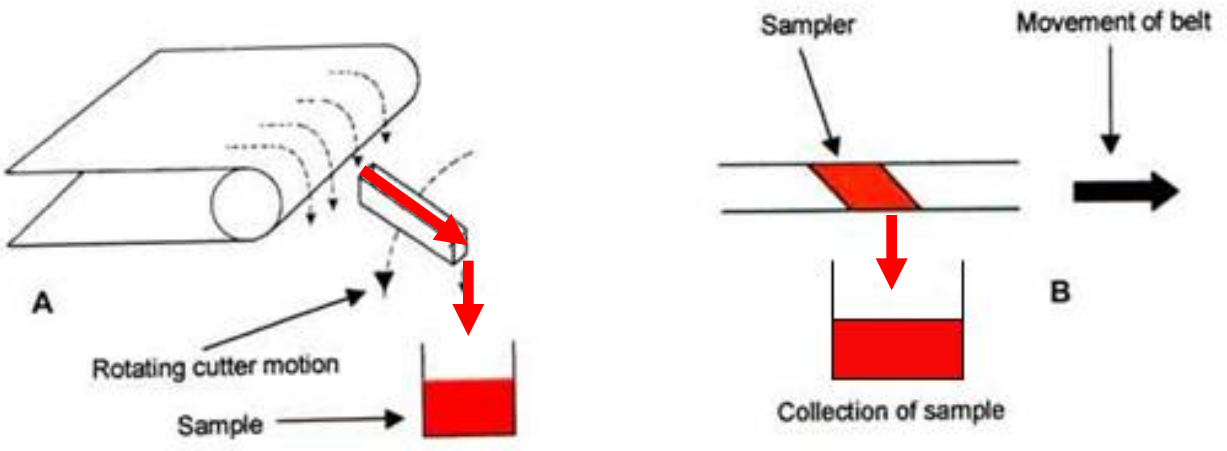


Fig 2.22 – sampling from conveyor belts

Figure (2.22) shows two possible scenarios for sampling directly from conveyor belts. In 'A' the sample is being cut automatically from the end of the belt, however this is only feasible if the belt is moving slowly. The dimensions of the cutter must be such as to be able to accept any of the particles (lumps) travelling along the belt

In 'B', the sampling device is also being operated automatically so that the movement of the belt is not affected. By stopping the belt periodically, it is possible to take a cross section sample manually but now at 90 ^{0} to the direction of movement of the belt.

Sampling of pharmaceutical tablets & powders

Because of the strict regulation under which the pharmaceutical industry exists, all routine pharmaceutical analysis has to be performed in accordance with a strict set of rules. Each analysis, which includes the sampling, has to be carried out using the **SOP (standard operating procedure)** for that analysis. This analysis procedure is established following extensive research and development, such that the method used for the analysis, is capable of achieving the required objective. This could be for example, the formal identification of a precursor used in the manufacture of a drug substance, or the analysis of a final drug product to BP (British Pharmacopoeia) specification.

Given the nature of the materials to be sampled, great care must be taken both in the choice of the location where sampling will take place and in the precautions needed to protect the sampler. The sampler may be required to wear special protective clothing and where feasible, sampling should be carried out in an area dedicated to the task. This dedicated area could well be a closed cubical within a warehouse. **It is imperative that contamination both to the sample and to the bulk material, are avoided during the process of sampling**

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Sampling within the pharmaceutical sector is carried out for a variety of purposes including:

- Acceptance of consignments;
- Batch release testing;
- Process control;
- Inspection for customs clearance;
- Deterioration;
- Adulteration.

Materials to be sampled will include:

- Starting materials for use in the production of pharmaceuticals;
- Intermediates in the manufacturing process;
- Pharmaceutical products;
- Packaging materials.

Although generic sampling procedures are just as important here as in other areas of sampling, given the final destination of the products from pharmaceutical manufacturer, guidelines have been established to aid the sampler. **These are illustrated on the next slide**

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Sampling guidelines for three sampling situations

For a uniform material obtained from a recognised supplier, and present as a single batch in 'N' separate sampling units, it would normally be appropriate to select 'n' or 'p' units from the batch for sampling. The value of 'n' or 'p' being obtained from the equations (2.1) or (2.2) :

Equation (2.1) $n = \sqrt{N} + 1$ [where full quantitative analysis is required]

Equation (2.2) $p = 0.4\sqrt{N}$ [where only confirmatory identification is required]

The sampling units from which increments would be selected would be chosen randomly. Those samples taken would then be placed in separate containers for initial visual inspection. Assuming no apparent difference between the samples, then the samples would be composited and a single sub-sample then selected for full analysis.

For a suspected non-uniform material obtained from an unrecognised source, a larger number of samples need to be taken. Increments would initially be taken from all of the 'N' sampling units, placed in sample containers and tested for identity. Providing the results are concordant, then 'r' sampling units are chosen randomly for sampling, where 'r' is calculated from equation (2.3):

Equation (2.3) $r = 1.5\sqrt{N}$

All 'r' samples are then supplied for analysis.

Fig 2.23 - typical drum container for tablets and powders

Figure (2.23) shows a typical drum used to contain tablets and powders. It is made from thick cardboard, is lined with plastic and has metal strengthening rings top and bottom.

Given that most products to be sampled should have little variability, it should not be necessary in most cases to use sampling devices designed for cross-sectional or variable depth sampling. Most sampling is therefore carried out by using stainless steel scoops of the types shown in figure (2.24). The size of the scoop will relate to the specific sampling task.

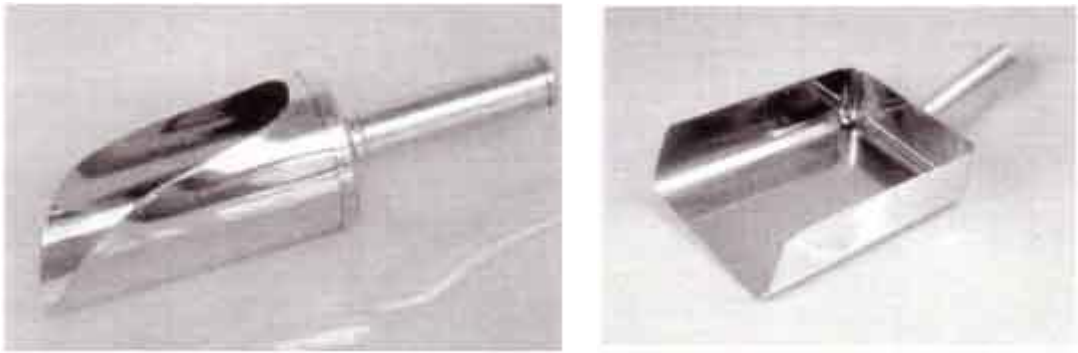

Fig 2.24 – stainless steel scoops

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Example sampling plan for solid pharmaceuticals

The succession of steps shown on this and the next slide are an example of a sampling plan suitable for the sampling of pharmaceutical tablets and powders

Example (2.i)

1. Read and digest the precautions that need to be observed when handling the material to be sampled
2. Obtain all of the equipment necessary for the sampling process and check that it is clean.
3. Locate the consignment to be sampled, count and record the total number of containers (sampling units).
4. Carefully examine all of the containers and record any obvious differences or damage. Check that all of the labels are intact and that all of the containers appear to be correctly labelled. Record any faults.
5. Separate any containers identified as faulty. These can be dealt with separately.
6. Check that all containers have the same batch number. Separate any with different batch numbers for sampling at a later time.
7. Give each of the remaining containers an individual number.
8. Randomly select the containers to be sampled and record the decision.
9. Carefully open a chosen container and inspect the contents. Record observations.
10. Assuming that cross-sectional or depth sampling is not required, select a sample from the top of the container using the recommended size sampling scoop.

Continued on the next slide

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11. Transfer the sample to a sample container. Divide this sample into two portions – one to be retained and the other to be sent for analysis. Seal the sample containers and label.
12. Reseal the sampled container and label to the effect that a sample has been removed.
13. Clean the sampling equipment as appropriate, observing all necessary safety precautions before sampling the other chosen containers.
14. Repeat steps 9 – 13 for all of the other containers that need to be sampled.
15. Finally clean all of the sampling equipment and leave dry for the next sampling exercise.
16. Deliver the samples to the laboratory for analysis and report any significant observations.
17. Decide or seek advice as to what needs to be done with the containers separated in steps 4 and 5 of this sampling plan.

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Sampling of solid materials - reflection

- There are a multiplicity of solid matrices that require sampling for analytical purposes. Each poses a unique problem and there is no single generic sampling procedure that can be used to sample all of these matrices.
- All solid matrices should be considered as heterogeneous although the degree of variability will depend on the matrix and it's situation. Pharmaceutical products should exhibit very little variability.
- Soils for the eventual analysis of non-volatile analytes, should be dried and ground to a particle size less than 2mm before analysis is attempted. The depth from which the soil sample is taken will depend on the reason for the analysis.
- The sampling of solids transported by lorry, ship, railway wagon etc. poses a major problem for the sampler. If possible, sampling should be attempted whilst the material is in motion, for instance being moved on a conveyor belt. Static heaps of less than 1 tonne can be sampled by the process of imaginary sectioning however this is an inherently inaccurate process and is unlikely to produce a truly representative sample.
- The tools used for sampling solid materials, particularly scoops, must be capable to accepting the largest of the particles (lumps) in the consignment.
- The sampling of pharmaceutical powders and tablets require the sampler to follow a strict set of procedures as set out in the prescribed SOP -**standard operating procedure.**

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Sampling of liquids

In theory, liquids pose less of a problem for the sampler than do solids, because of the possibility of being able to achieve total homogeneity. In practice however, liquids for sampling can only be considered homogeneous, when they can be seen to be single phase and when they can be thoroughly mixed prior to sampling. Oceans and deep-water lakes for instance will show differences in composition due to differing in densities, slow flowing rivers will exhibit composition differences across the width of the river. Tankers, drums etc., where the liquid inside cannot be seen by the viewer, could contain multiple liquid phases. Some example of differing sampling situations are shown below:

- Sampling of liquids flowing within defined boundaries
- Sampling of water from oceans and deep-water lakes
- Sampling of water from open locations – small lakes, reservoirs & ponds
- Sampling of liquids stored in closed containers

Examples covering these four situations will be covered in the next batch of slides

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Sampling of liquids flowing within defined boundaries

Slow moving liquids, flowing within confined boundaries, flow at differing rates dependent upon their position with respect to the boundary (wall of a pipe or banks of a river or canal, for instance). The process is termed **Laminar Flow,** with the liquid furthest away from the boundary flowing at the fastest rate and with zero flow being apparent at the boundary edge. It is therefore necessary, in order to take a representative sample, to induce turbulence into the flow pattern. In pipes, this can be done in a number of ways, one of which is illustrated in Figure (2.25).

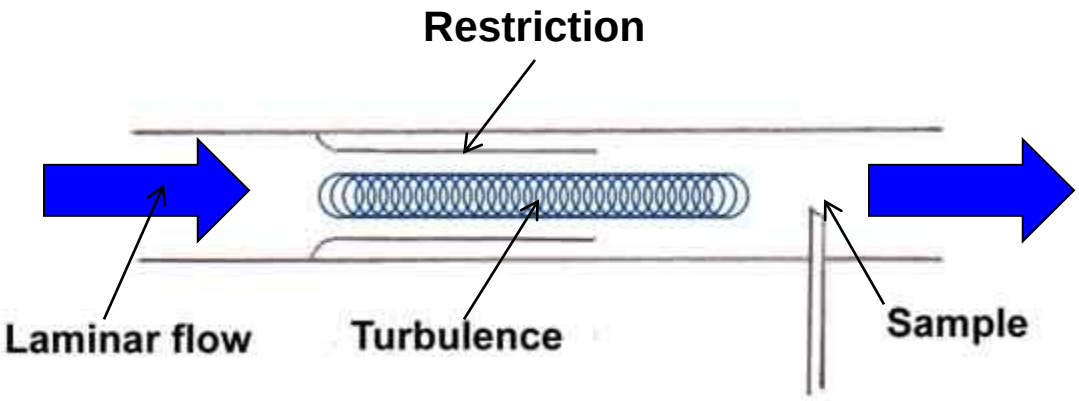

Figure 2.25 – sampling of liquid from a pipe

As indicated in Figure (2.25), the liquid flows in a laminar manner until it meets the restriction in the pipe, when it will become turbulent. The sample is taken from within the turbulent zone. After the turbulence the liquid returns to laminar flow conditions.

Note: the next slide shows an alternative way of creating turbulence

Sampling of liquids on chemical plants

Figure 2.26 – typical chemical plant

A chemical plant producing liquid products will have many places where accurate sampling will benefit the efficiency of the process. Figure (2.26) shows four fractionating towers where sampling and analysis will be routinely carried out. One of the features of a modern chemical plant is that sampling and subsequent analysis are performed automatically, thereby removing the time delay associated with sending samples to a dedicated laboratory for analysis. Liquids flowing through pipes on the plant will also need to be sampled and if the flow rate is slow, turbulence will need to be introduced. An alternative means of achieving this turbulence is shown Figure (2.27). In this example, the turbulence has been created by introducing a right angled bend into the pipe, just ahead of the sampling point. The sample would be taken directly to the analyser.

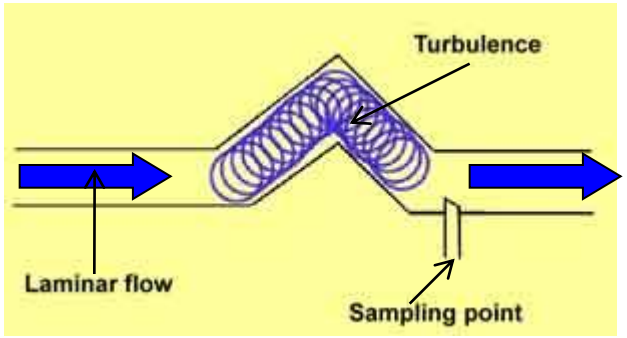

Figure 2.27 – schematic diagram of liquid flow through a pipe

Sampling of water flowing within defined boundaries

Figure 2.28 - slow flowing river

Figure 2.29 – fast flowing river

A fast flowing river as illustrated in figure (2.29), will generate its own turbulence and thus will require no artificial means of mixing the water. A single water sample will therefore constitute a representative sample. Figure (2.28) on the other hand shows a slow flowing river where several water samples would need to be taken across the width of the water course, and these composited and sub-sampled, in order to produce a similarly representative sample. Samples would generally be taken by utilising a 'dipping process', using a clean open glass container (eg: a beaker or a special sampling bottle) and transferred immediately to a clean glass or plastic stoppered bottle. It must be recognised that organic pollutants (eg: volatile organics), due to poor miscibility, will tend to concentrate at the surface of the water course and thus sampling in this way could produce a sample rich in organic pollutants.

Sampling of water from oceans and deep water lakes

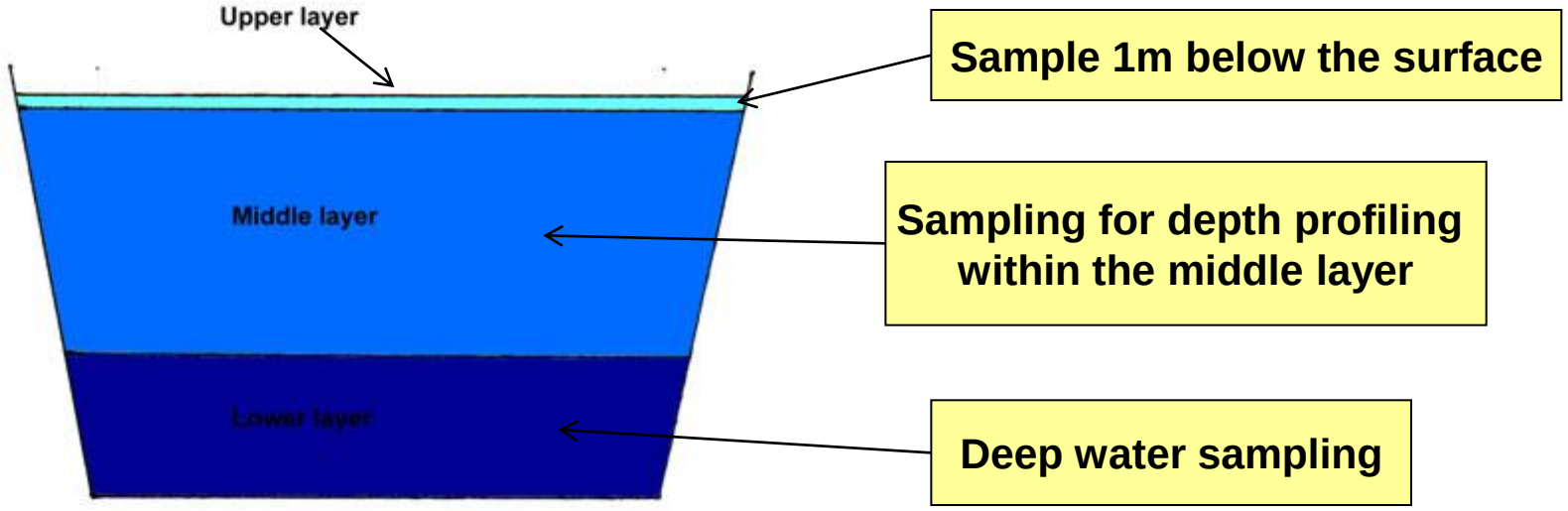

Figure 2.30 – layer structure of deep waters

Given that many possible organic contaminants in water are both inherently insoluble and have a lower density than water, they will tend to concentrate within the surface layer. Taking samples that include this layer are therefore likely to be unrepresentative of the bulk. As the depth of the water increases, the density also increases, resulting in a lower layer that tends not to mix with the water above it. The consistency of this layer is considered to be reasonably constant. The middle layer is subject to wave and tidal influences but may show some slight changes in composition with depth

In order to avoid the upper water layer, which could be concentrating insoluble or partially insoluble organic contaminants, the sampling of ocean or deep lake water is recommended to take place at about 1m below the surface. Although a sampling bottle of the type shown in figure (2.7) could be used, it is preferable to use a remote sampling device as illustrated in figures (2.31 and 2.32).

Figure 2.31 – Kevlar sampling tube

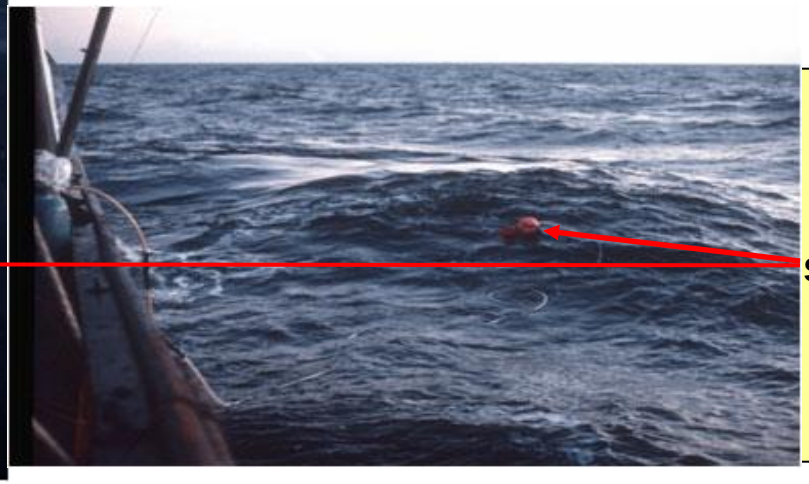

Figure 2.32 – ocean sampling at a 1m depth

Figures (2.31 & 2.32) show the sampling tube and sampling point below the buoy

Figures (2.31) & (2.32) show 'Kevlar' tubing being used the sample water at a depth of about 1m below the Ocean's surface. The sampling point is away from the hull of the vessel to avoid possible contamination due to corrosion. The sample is pumped directly into a clean laboratory situated on the deck of the vessel.

Sampling of water from open locations – small lakes, reservoirs & ponds

The water quality in small lakes and ponds, often used for angling, sometimes need to be measured when problems manifest themselves (for instance fish dying or not growing as fast as normal or the presence of excess algae). Some measurement of water quality (eg: pH or dissolved oxygen) can be made on the water directly without the need for sampling, however most measurements will require water samples to be taken and subsequent measurements made in the analytical laboratory.

Figure 2.33 – small pond used by anglers

The pond as shown in figure (2.33) should preferably be sampled from a central location rather than from a convenient point on the edge of the pond. This will thus require the sampler to have available a small boat or dingy from which to capture the sample. Safety precautions would need to be taken, so as to avoid unforeseen accidents. Recommended sampling locations are shown in red.

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Sampling of liquids stored in closed containers

Figure 2.34 – petrol tanker

This sampling situation relates to liquids stored or transported in tankers, drums etc. A tanker (figure 2.34) or a drum of liquid will each represent a single 'sampling unit' as defined earlier in this element. As it is not possible to view the inside of the container the person taking the sample has to assume the liquid to be multiphase, possibly containing suspended particulate matter. Liquids stored in large tanks (road, rail or ship) should if possible have an agitator built into the tank to facilitate mixing of the contents prior to sampling. Assuming that no such agitator exists then sampling equipment must be used that allows for depth profiling to be achieved.

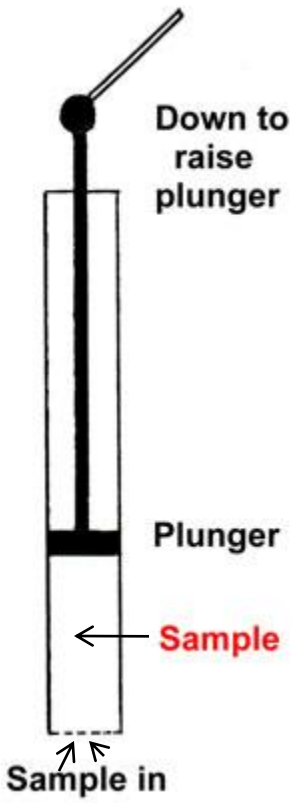

Figure 2.35 – device for sampling liquids at various depths

In the case of petrol tankers and tanks holding petrol/diesel in garage forecourts, the main problem is likely to be water accumulating at the base of the tank. Sampling devices need to be available to take samples from the base of the tank whilst avoiding too much of the fuel above. A suitable device is shown in Figure (2.35). The device is inserted into the tank of liquid with the plunger at the base of the device. The plunger is then raised by pulling on the handle which draws liquid through a mesh membrane into the sampling chamber. The sample can then be removed and additional samples taken at other depths. The sampling device would need to be calibrated such that the depth at which the sample was taken could be recorded

Note: a sampling device suitable for depth profiling within drums was described earlier in this Chapter and is illustrated in figure (2.9)

Sampling of liquids - reflection

- In achieving a representative sample, liquids in theory pose less of a problem than solids. However this is only the case where small amounts of liquid are being handled in transparent vessels and thus can be easily shaken to effect homogeneity.
- It is frequently necessary to sample large volumes and areas of water and in these circumstances the sampler must be aware of the principles of laminar flow, where the water is flowing within confined boundaries.
- Slow flowing liquids in pipes, need to be homogenised by creating turbulence in the flow pattern.
- Differing concentrations of analytes can occur at differing depths in deep ocean situations and special equipment must be used to capture samples at differing depths.
- Liquid tankers and drums may well contain liquids which are immiscible. In these circumstances it is necessary to utilise sampling equipment that allows for depth profiling or allows samples to be taken at selected depths.
- In some cases, liquid samples can be transferred directly to an analyser to speed up the generation of analytical information.

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Sampling of gases, vapours & aerosols

Within this sampling category we have a number of sub-species. These include:

- **Gases** – classed as molecular in size and which do not condense at room temperature;
- **Vapours** – produced from volatile liquids and which will begin to condense if the concentrations are high;
- **Particulate matter** – any material that exists as a solid or liquid in the atmosphere. This includes solid particles (eg: carbon particles from diesel engines) generally referred to as ‘dust’, or liquid droplets (eg: water, oil) that are classed as ‘mists’ and aerosols. Aerosols are groups of particles in either a solid or a liquid state that are small enough to remain suspended in the atmosphere. (eg: inhalers for asthma sufferers)

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Much gas sampling is undertaken for environmental purposes to monitor atmospheric air quality and air quality within confined workspaces. Given that we are normally unable to see what we have to sample, the assumption is generally taken that the air to be sampled is homogeneous, **at the time and point at which the sample is taken**. The main problem with the sampling of gases is not the taking of the sample itself, but in its storage prior to analysis.

Gases stored under ambient conditions in suitable containers can take up large volumes of space and any subsequent changes to temperature and pressure can alter the integrity of the sample. For instance, a sample taken at above ambient temperature could lose its less volatile components by condensation, if the temperature of the sample were to be lowered to ambient. Under these conditions and in order to maintain the sample's integrity, it would be necessary to return the sample to its original temperature before taking a portion of the sample for analysis.

The other problem with gases is the low molecular concentrations that exist in gaseous environments when compared to the condensed phases of solids and liquids. The molar volume of any gas (volume containing 1 molecular mass) under given temperature and pressure conditions remains constant. At $20^{o}C$ and 1 atmosphere pressure, for instance, the volume occupied is approximately 24 dm^3

Where possible, most atmospheric air sampling and other air and gas sampling protocols involve a combination of sampling and analysis so as to avoid the necessity of storing the samples. **The sample is thus taken and passed directly to the analyser**. Examples where this occurs includes environmental air quality monitoring for CO, SO_2, and NOX (oxides of nitrogen). This provides **'real-time' analysis data** as opposed to a **time-weighted average** **(TWA)** for samples collected over a period of time.

Figure 2.36 - crematorium

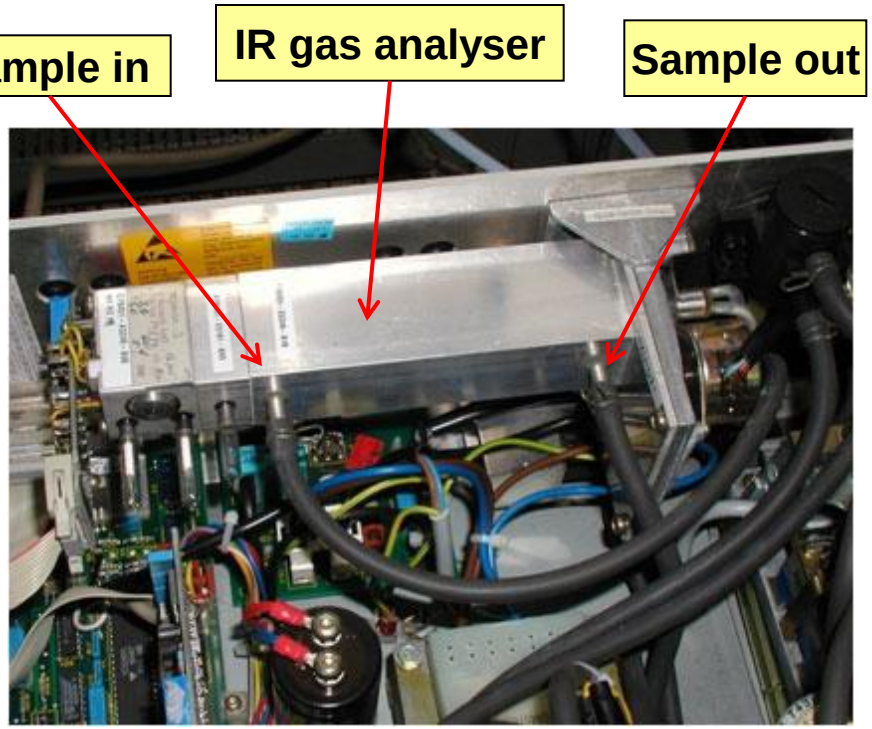

Figure 2.37 – on-line IR gas analyser

Figures (2.36) & (2.37) show the chimneys of a crematorium and an infra-red gas analyser which continuously monitors the CO content of the emitted gases. The crematorium has to comply with regulations on emissions of CO laid down by the local council.

Atmospheric sampling

For investigative or non-routine analysis or monitoring, that is to be carried out within a laboratory, we need to have available, equipment that is suitable for capturing and storing gas samples. There are two approaches that may be adopted dependent upon the target gases that are to be measured.

- Gases may be collected and stored – generally referred to as '**Grab sampling**'
- Gases may be passed through absorbing or adsorbing mediums over a period of time so that the target analytes are trapped into or onto the medium. The resultant solution or reagent is then transferred to the laboratory for measurement of the target analytes. This technique is sometimes referred to as '**continuous sampling**'.

Grab samples give a measure of the analyte concentration at a defined time. Continuous sample on the other hand produce a '**time weighted average**' concentration, over the period of time that the sample was collected.

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Grab sampling of gases, vapours & aerosols

Definition of 'grab sampling'

Refers to any sampling procedure that collects a single sample at a particular point in time

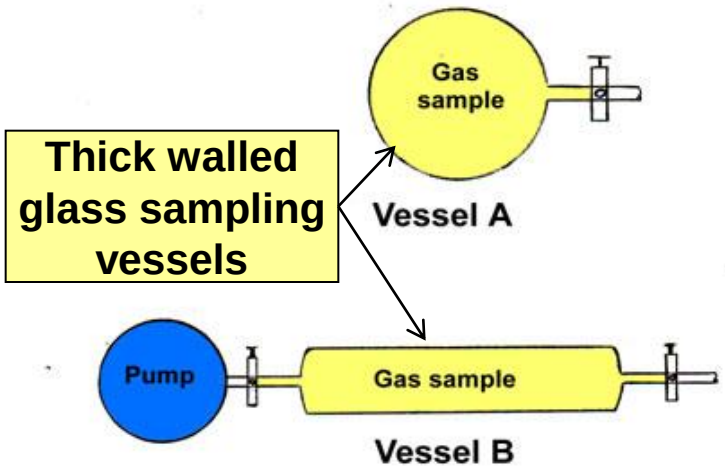

Figure 2.38 – gas sampling vessels

The sample may be collected in a flask (glass or stainless steel), plastic bag or any other suitable container. Two typical flasks are illustrated in figure (2.38). Taps are made from metal or ground glass and are not greased

The vessels shown in Figure (2.38) would be typically 250 – 1000 ml in volume. Vessel **A** is evacuated in the laboratory and the tap opened to collect the gas sample. Once atmospheric pressure inside the vessel has been reached, the tap is then closed to store the sample. Although vessel **B** could also be used in the vacuum collection mode, the sample would generally be drawn through the vessel by applying slight vacuum at one end with both taps opened. When a representative gas sample has been collected, the tap closest to the pump is then closed, fractionally before the tap on the other side. This will ensure that the sample is stored at atmospheric pressure.

Taking analysis samples of gases, vapours & aerosols

These types of gas sampling vessels are perfectly adequate for qualitative analysis however care must be taken when attempting to use them for high accuracy quantitative measurement. The problem lies in the taking of a test portion of the sample for analysis. Figure (2.39) illustrates the situation whereby a small sample is being removed for the type A vessel.

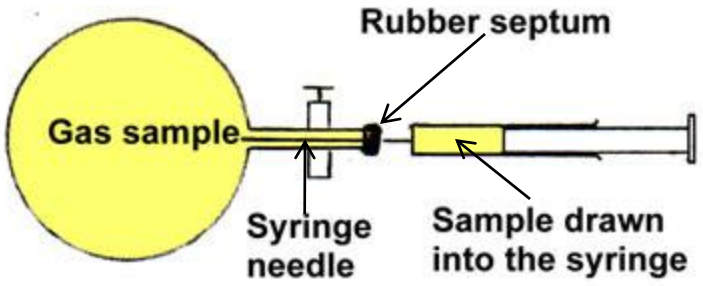

Figure 2.39 – taking an analysis sample

A rubber septum can be placed over the end of the sampling vessel and the tap turned to the open position. A specialist gas sampling syringe is then inserted through the septum and a portion of the gas sample removed for analysis. The sample in the syringe is then analysed immediately, probably by a gas chromatographic method. [see Chapter 7 of this teaching & learning programme]

It must be realised, that having removed a small quantity of the gas from the sampling vessel, this has now created a slight vacuum within the vessel. So the next sample to be taken for say replicate analysis, will be slightly less than the previous. Assuming that the volume of gas taken for analysis is not in excess of 1 cm^3 and that the total volume is in excess of 500 cm^3, then the slight error will be acceptable.

Having captured a sample in vessel type ‘B’ [Figure (2.38)] it is possible to dispense this sample for analysis by using a liquid displacement technique as illustrated in Figure (2.40)

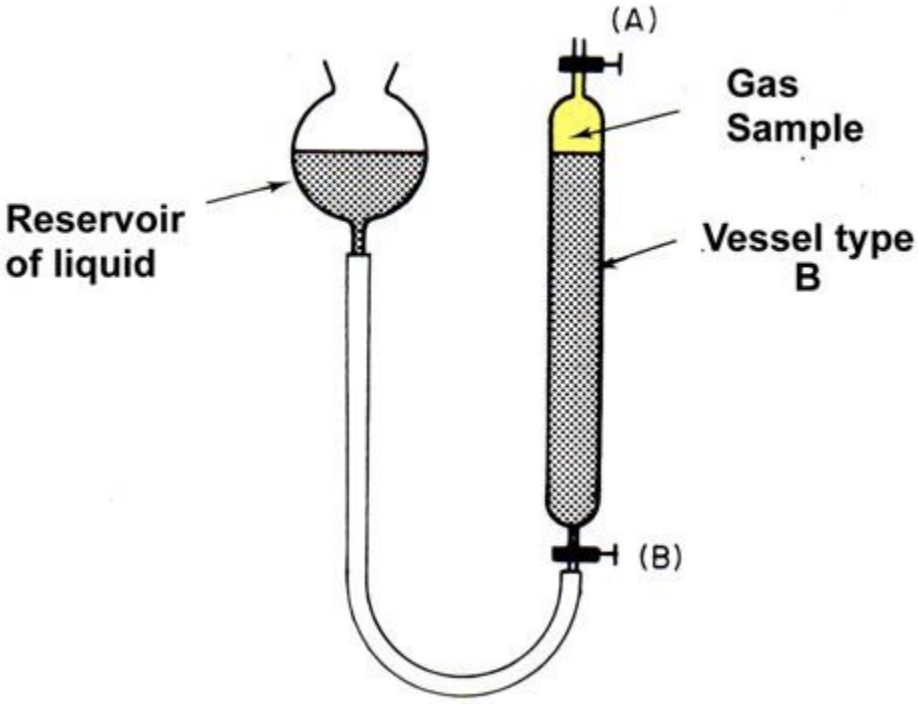

Figure 2.40 – taking a sample for analysis

The vessel type ‘B’ is attached as shown in Figure (2.40) to a reservoir of liquid in which the gaseous components are known to be insoluble. Mercury is the best liquid to use, however due to its potential toxicity other less toxic substances are generally employed. By opening gas tap ’B’ at the base of the vessel and by adjusting the height of the liquid reservoir, the gas in the vessel may be pressurised. A small septum may be placed over the end ‘A’ and the tap ‘A’ now opened. By using a syringe as illustrated in Figure (2.39), a test portion of the gas can now be removed. The sample in the syringe, initially will be under slight pressure, however on removal from the septum, the test portion will rapidly attain atmospheric pressure. Replicate test portions can be taken by using a similar procedure

Grab sampling using ‘Draeger’ type tubes

Dreager tubes (from the initial inventor of this sampling and analysis system) are gas detector tubes for use in workspace monitoring and other industrial applications. Tubes are available to sample and measure around 160 different analytes, although analytical sensitivities very considerably from ppm (parts per million) concentrations for some analytes to % concentrations for others. Typical tubes are shown in Figure (2.41). The tubes are constructed from glass, are up to 10 cm long and contain an analyte specific reagent adsorbed onto an inert solid support. The tubes are calibrated and the reagent changes colour as the contaminated air is drawn over the adsorbent. The change in colour is an indication of the concentration of the analyte in the atmosphere provided the volume of gas drawn through the tube is accurately controlled. These devices are generally used with hand-held pumps of the types shown in Figures (2.42) and (2.43)

Figure 2.41 – Draeger tubes

Figure 2.42 – piston pump

Figure 2.43 – bellows pump

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Continuous sampling of gases, vapours & aerosols

Continuous sampling refers to the situation where the gas sample is captured over a period of time and thus the final analytical result will be a historic **time weighted Average (TWA)** concentration over the period of time that the sample was captured. There are two forms of continuous sampling – **active** and **passive.**

Both sampling modes allow for very low concentrations of gases or vapours to be measured, much lower than would be measurable by using a grab sampling technique.

In the **active** mode, a pump is used the draw the sample through an absorbing chemical reagent or over a solid adsorbent such as active charcoal. This form of sample collection is appropriate for the measurement of reactive chemicals and particularly volatile organic compounds (VOCs).

In the **passive** mode, the sample is captured over a long period of time by natural diffusion of the analyte onto a suitable adsorbent. Sampling times would not usually be less than 8 hours and could be several days.

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Active mode sampling

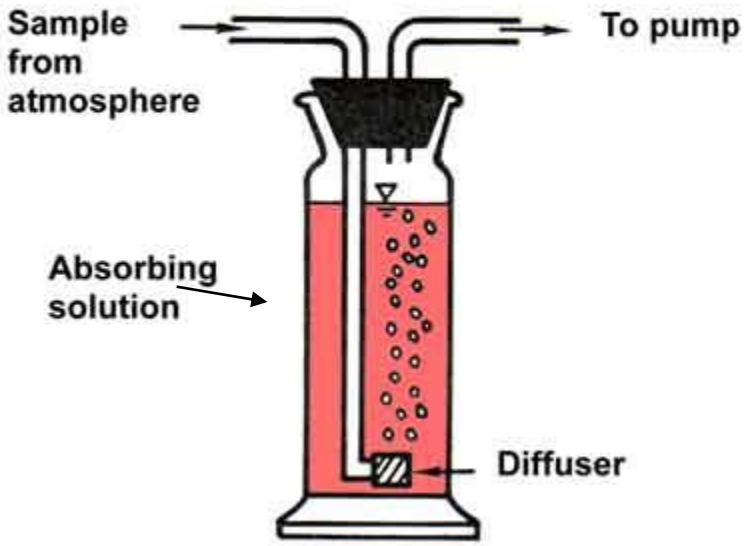

Figure 2.44 – 250 or 500 cm Dreschel bottle

A known volume of gas is drawn slowly through the reagent/absorbing solution. The gas is dispersed to small bubbles in order to maximise the surface area contact with the liquid. When using volatile solvents It may be necessary to cool the reagent to reduce evaporation.

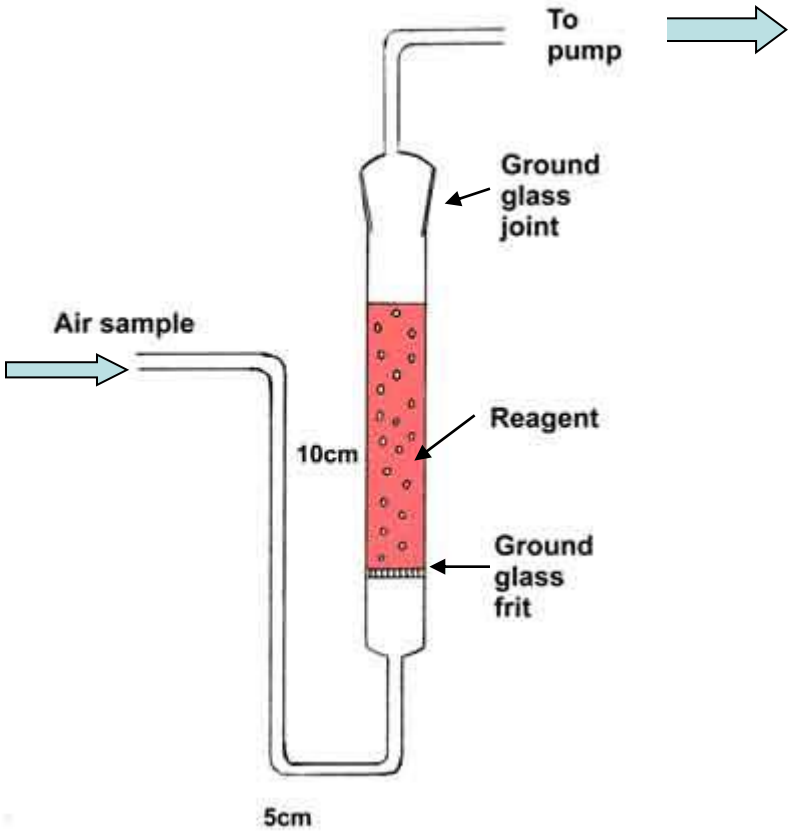

Figure 2.45 – typical sample impinger

With low solubility gases or vapours, it may be necessary to have more than one absorption device connected in series in order to capture all of the target analyte.

Although gas absorption systems as illustrated in figures (2.44 & 2.45) are easy to set up and to use within a laboratory, they are inconvenient to use outside the laboratory environment. A more convenient approach is to use solid adsorbents that are designed to target either single or groups of analytes. Typical sampling devices are made from glass tubing and contain either generic (eg: active charcoal), or specific adsorbents. A typical charcoal tube is shown schematically in Figure (2.46).

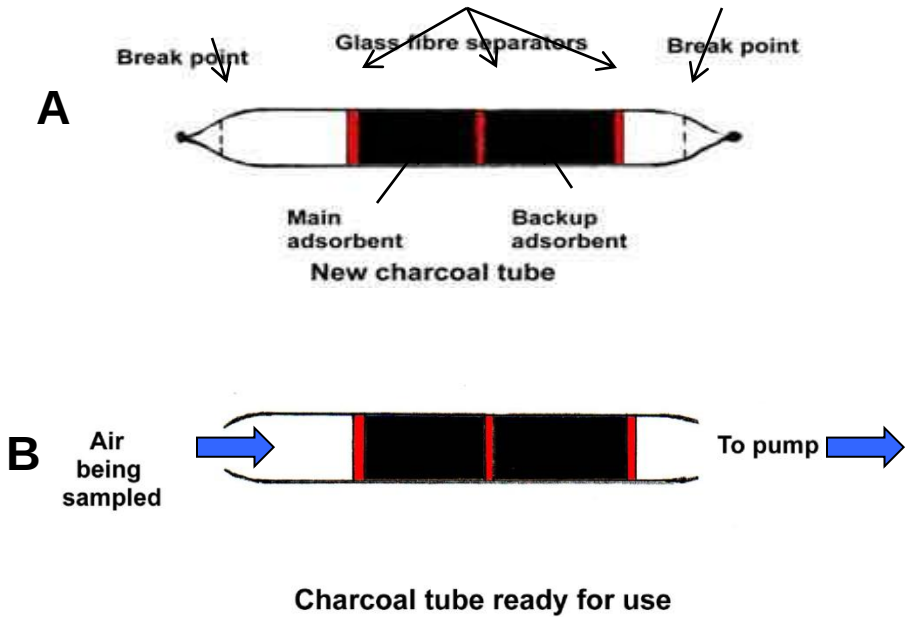

Figure 2.46 – charcoal adsorption tube

Figure (2.46) shows a schematic diagram of a typical charcoal tube used for sampling organic vapours in the atmosphere. The glass tubes come in a number of sizes with dimensions of 60mm in length and 5mm diameter being typical. The tube is initially sealed as shown in (A) and contains two portions of activated charcoal. To use the tube, the end seals are removed and the tube attached to a small pump with flow control. The air sample is drawn through the tube as indicated for a fixed period of time. After sampling, the tube is capped to secure the sample and sent to the laboratory for analysis.

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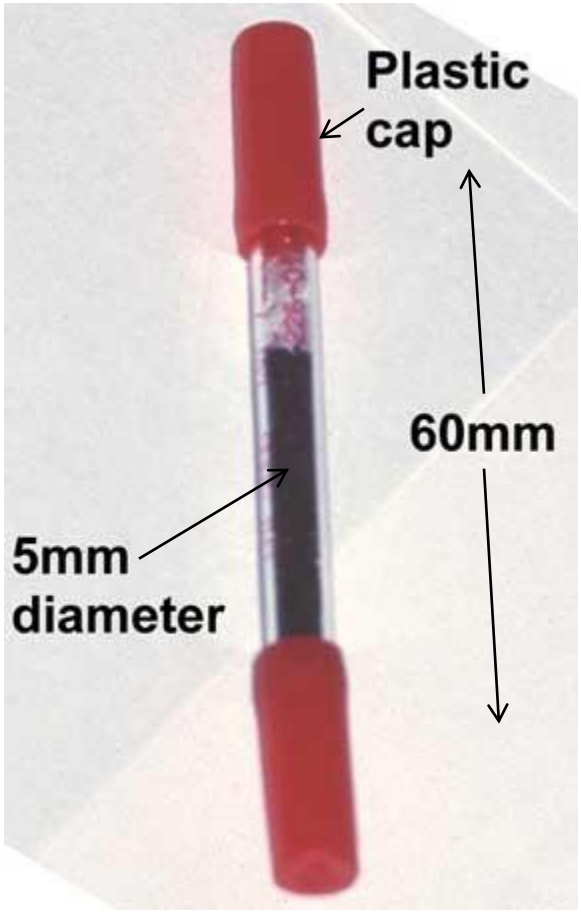

Figure (2.47) shows a tube capped and waiting to be sent for analysis. The two parts of the adsorbent are separated and the analyte(s) chemically desorbed ready for analysis by gas-liquid chromatography. [See Chapter 7 of this teaching and learning programme]. If the back-up portion of the adsorbent is shown to contain a substantial quantity of the analyte, then the analysis has to be repeated as the concentration of analyte in the atmosphere is too high for the adsorbent and a representative sample will not have been captured.

Figure 2.47 – tube ready for analysis

Passive mode sampling

The term '**passive sampling**' refers to a sample being taken over a long period of time by the process of natural diffusion of the analyte onto a suitable adsorbent. Figure (2.48) is a typical stainless steel diffusion sampling tube. Figure (2.49) is a schematic representation of the inside of the tube.

Figure 2.48 – stainless steel passive sampler

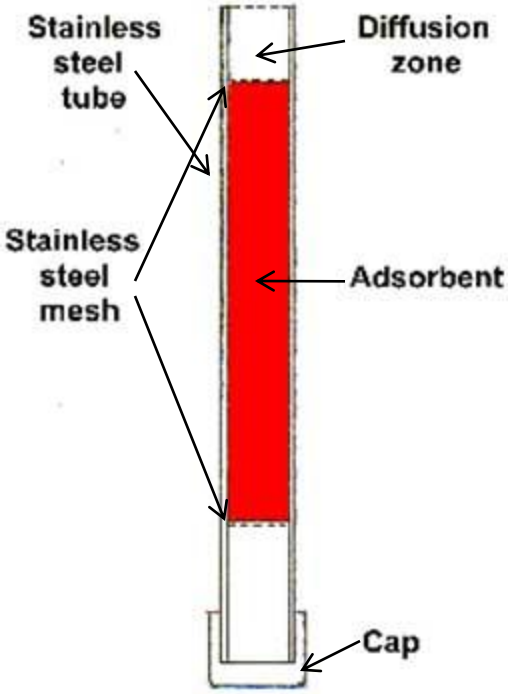

Figure 2.49 – schematic diagram of passive sampling tube

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The tube as illustrated in figures (2.48 & 2.49) is packed with a suitable adsorbent (Tenax – a porous polymer is often favoured) and held in place with small pieces of stainless steel mesh. The tube is capped at both ends until required. For continuous monitoring the top cap is removed, the tube placed in position and the time recorded. The target analyte(s) diffuse across the diffusion zone and are captured by the adsorbent. The rate of diffusion is controlled by Fick's first Law of Diffusion, which states that "*substances will diffuse in accordance with the concentration gradient existing at the surface of the adsorbent".*

The graph shown in figure (2.50) illustrates what is meant by the term 'concentration gradient' in this context. The concentration at the surface of the adsorbent is assumed to be zero and that in the air, is either constant or variable. Following a fixed time period for sampling, the tube is again capped and sent for analysis.

These passive samplers require the adsorbed analytes to be thermally desorbed directly onto the front of a gas-chromatographic column for separation and analysis.

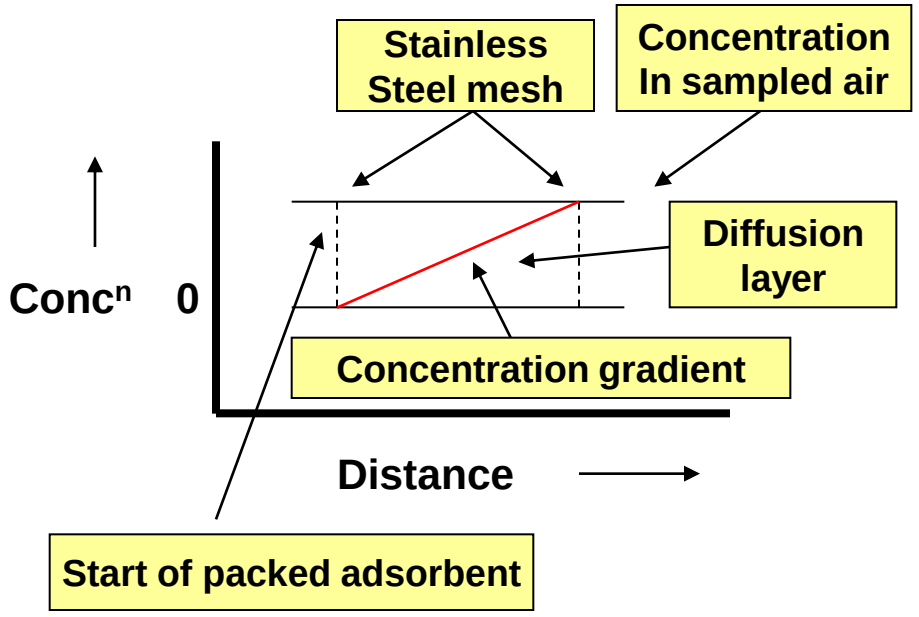

Figure 2.50 – illustration of concn. gradient

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Gas detector tubes (Draeger tubes) as illustrated in figure (2.41) may also be used in the passive mode as shown in Figure (2.51)

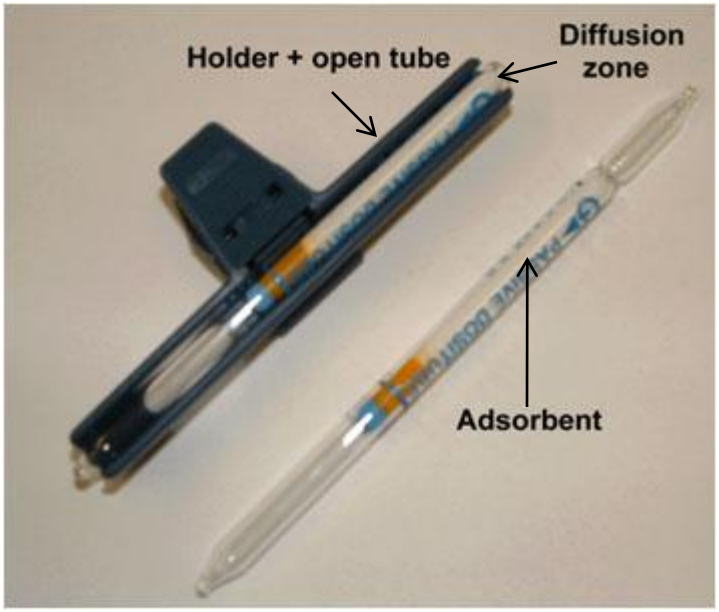

Figure 2.51 – Photographs of gas detection for use in passive mode

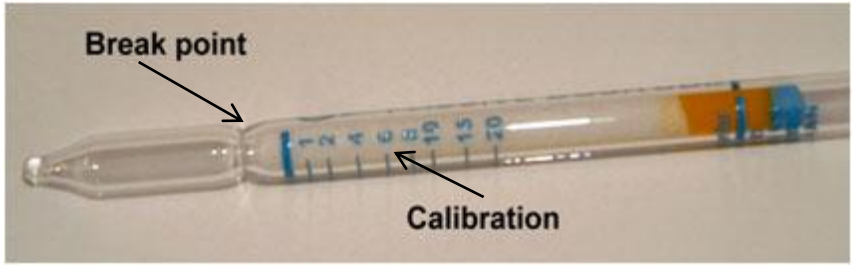

Figure (2.51) shows a typical calibrated gas detection tube, holder for the tube and operative having the tube close to his breathing zone. At the end of the sampling period, the tube will indicate the average concentration to which the operative has been exposed over the working period..

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Sampling of atmospheres for particulate matter

Introduction

Particulate matter covers a variety of particle sizes from between below 0.1 to greater than 100 μm diameter. Most sampling and analysis of particulate matter is of interest in the range below 100 μm, as it is particles within this range that can be inhaled into the body via the nose or mouth. This is sometimes referred to as the **Inhalable fraction** of the total particulates in the air. Within this inhalable fraction there are two more important sub-fractions – the **Thoracic fraction** and the **Respirable fraction**.

Definition of the 'thoracic fraction'

The mass fraction of inhaled particles penetrating the respiratory system beyond the larynx

Definition of the 'respirable fraction'

The mass fraction of inhaled particles that penetrates to the unciliated airways of the lung

Particles in the '**thoracic fraction**' have been shown to have diameters of between 1 – 30 μm, with a median of around 10 μm. Those in the 'respirable fraction' are smaller with diameters of around 1 – 10 μm and with a median of around 4 μm. Diseases such as pneumoconioses relates to the **respirable** fraction of particulate matter entering the lungs whilst incidences such as bronchitis and asthma may well be due to particulate matter within the thoracic fraction

Personal samplers for particulate matter

Sampling equipment has been designed to trap for identification purposes and to quantify where possible, particulate concentrations within both working and ambient air environments. Some of this equipment is for personal use and has been designed to be worn during a normal working day. These utilise small pumps similar in size to those used for gas and vapour sampling but with the air samples being drawn through glass fibre or membrane filters. The flow rate of air drawn through the filter will be around 2 $l.min^{-1}$ with the filter choice being dependent upon the type of analysis to be carried out. Figure (2.52) shows a schematic diagram of a typical filter holder and filter used for personal sampling.

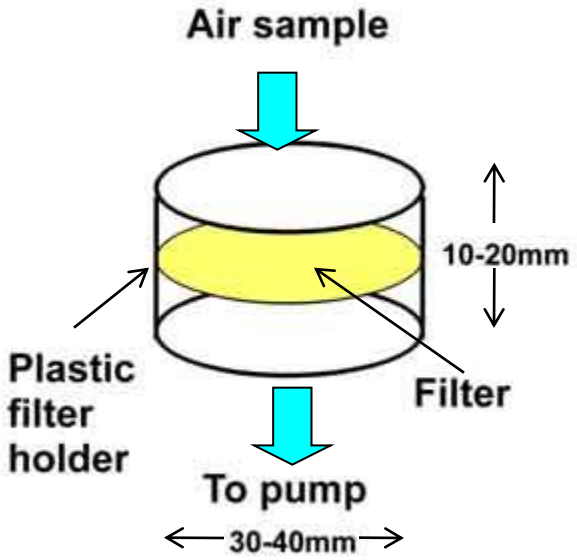

Figure 2.52 – schematic diagram of a personal sampler

For quantitative measurement, the filter is accurately weighed on a micro analytical balance and then transferred to the filter holder. The holder is clipped to the lapel of the industrial clothing and the pump attached around the waist. Air is drawn through the filter at a known rate for a fixed time. After sampling, the filter is removed and weighed again. A time weighted average value is obtained.

Figure 2.53 – cyclone personal sampler

The simple sampler as illustrated in figure (2.52) will collect all particulate matter above the pore size of the filter membrane. This would not therefore be able specifically identify the presence of those size particles which are most likely to cause health problems. The cyclone elutriator is capable of removing the larger particles, before they reach the filter membrane. As shown in figures (2.53 & 2.54) The dusty air is sucked into the device and spirals around a conical container such that the larger particles separate out and fall into the grit container at the base of the device. The air is then drawn through the membrane filter, which traps the smaller particles for analysis. The filter will again be weighed before and after sampling.

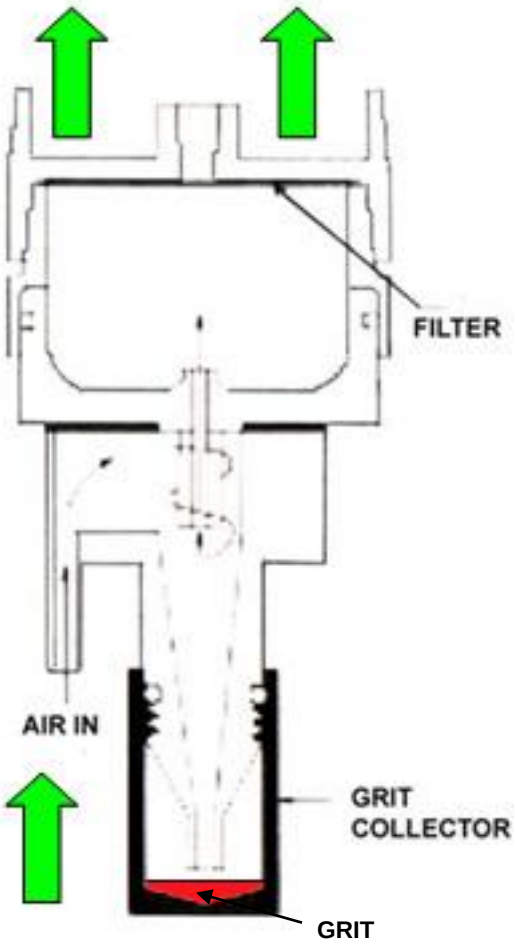

Figure 2.54 – cyclone sampler - schematic

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Continuous monitoring for particulate matter

For continuous monitoring of ambient air for quality assessment purposes, high volume samplers are usually employed. The particles of interest are often referred to as 'PM10s'. These represent particles with diameters of below 10 μm and so relate to the '**Thoracic**' and '**Respirable**' fractions of particulate matter. A schematic diagram of a typical high volume PM_{10} sampling device is shown in Figure (2.55).

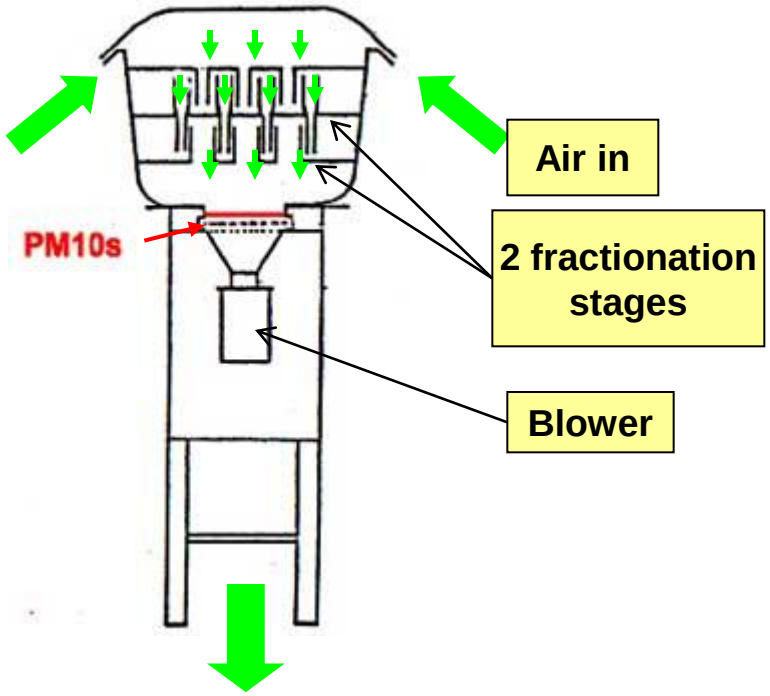

Figure 2.55 – high volume sampler

In figure (2.55) air enters at the top of the device and undergoes 2 stages of fractionation to remove the larger particles of diameters greater than 10 μm. The air containing the smaller PM_{10} particles is then drawn through the filter, which is weighed before and after sampling. Samplers of this type can draw through the filter at rates of 1 $m^3.min^{-1}$. Once again, a time weighted average concentration will be obtained.

Cascade impactors

Methods of sample collection so far described, use filters to remove particulate matter from the air being sampled. Cascade impactors offer a significant advantages over these simpler methods in that they allow particles to be fractionated according to their masses within a wide range of particle sizes (0.5 - 200 μm) and the various fractions measured. A schematic diagram of a typical cascade impactor is shown in Figure (2.56). As the flow holes decrease in size, the momentum of the particles increase until even the smallest particles can impact with the plates.

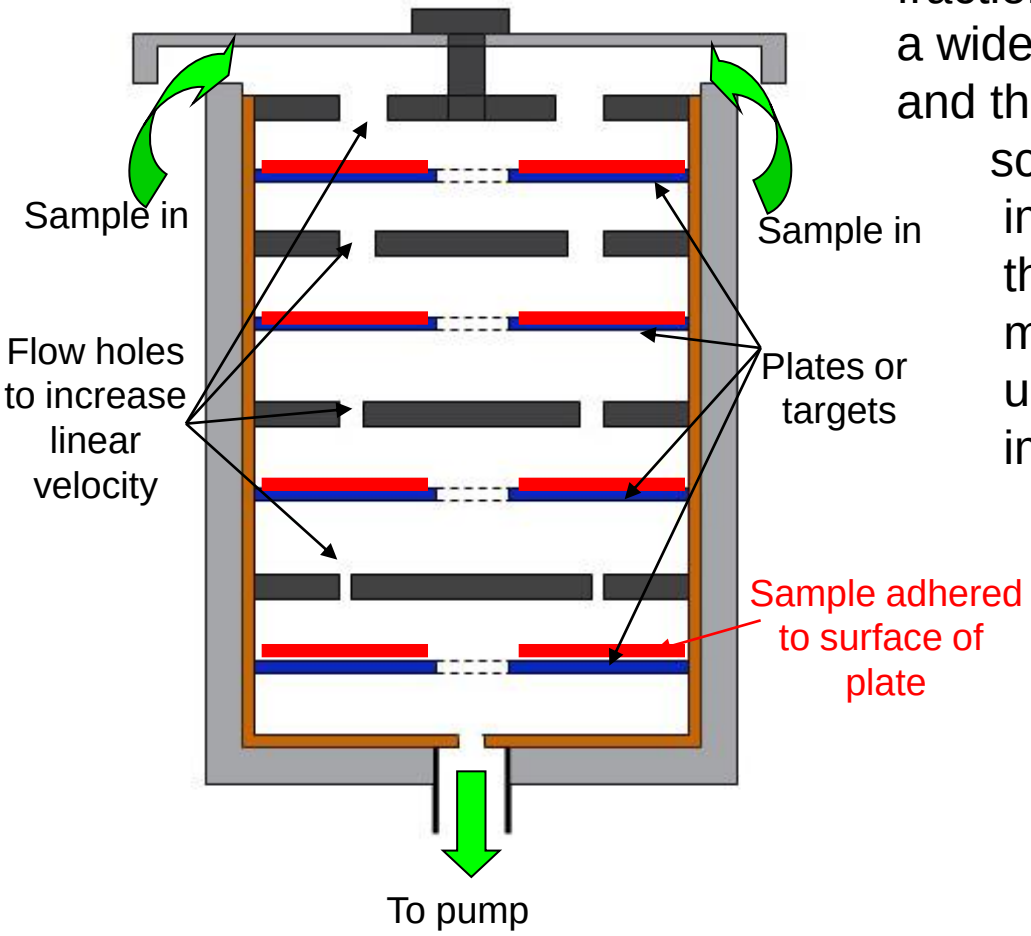

Figure 2.56 – cascade impactor

As indicated in Figure (2.56), air is drawn at a constant rate, through the device to impact on the plates (or targets) which are coated with petroleum or glycerine jelly. The smaller particles adhere to the plates lower down the cascade. After sampling, the device is de-mountable so that each plate may be separated for analysis.

Sampling of inhalers

Introduction

The pharmaceutical industry has produced a range of drugs that can relieve respiratory illnesses such as asthma. Delivery of these drugs is often via 'inhalers' as shown in Figure (2.57).

Figure 2.57 – typical inhaler

The inhaler as shown in Figure (2.57) is shaken vigorously for about 5 seconds. The mouthpiece placed in the mouth of the recipient and a shot of the canister's contents is fired directly into the throat by pushing down on the canister whilst breathing in at the same time.

The canister as shown in Figure (2.57), contains the active ingredient in the form of solid particles suspended in a suitable propellant. The propellant is a very low boiling point liquid. In order to control dosage and check long-term stability of the product, analysis of the canister must be carried out in such a way as to mimic as far as possible, the way the inhaler is used in practice. A modified cascade impactor is recommended for sampling prior to analysis and is illustrated on the next slide.

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Sampling of inhalers – use of cascade impactors

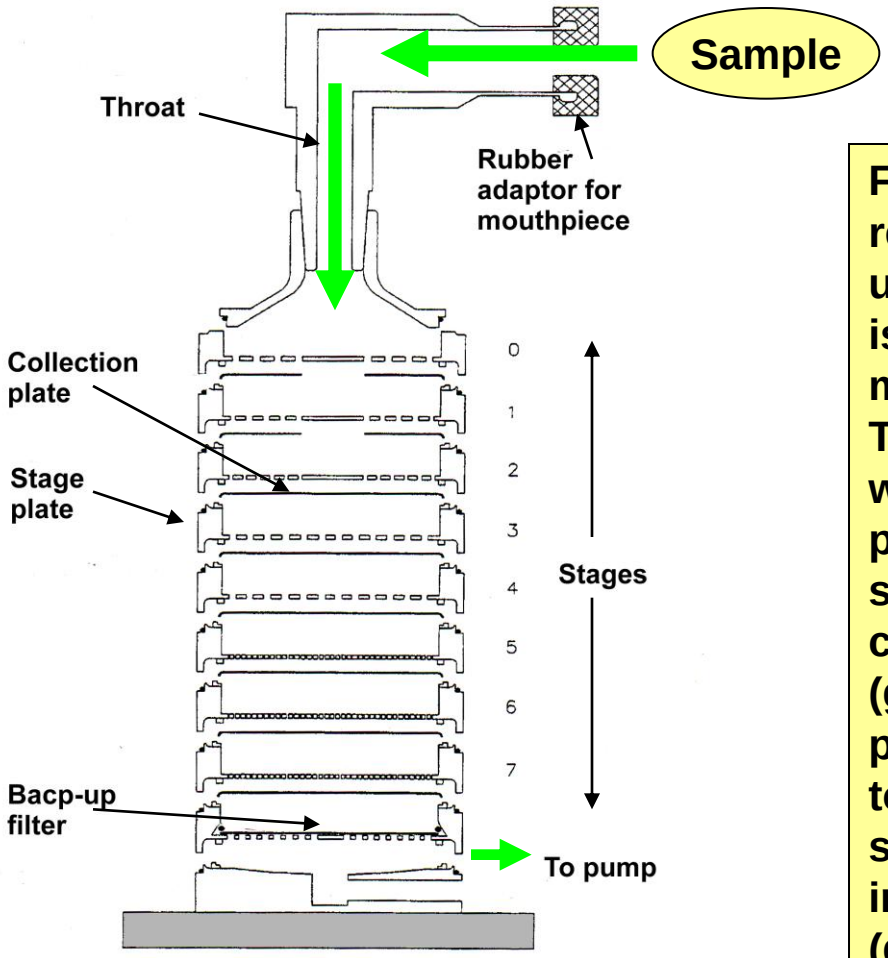


Figure 2.58 – cascade inhaler for the sampling of inhalers

The typical size of a cascade impactor is around 30 cm tall with a diameter of about 10 cm. The number of stages, can be selected to satisfy the sampling requirements.

Figure (2.58) shows a diagrammatic representation of a cascade impactor used for sampling of inhalers. The inhaler is shaken and fired through the mouthpiece into the top of the impactor. The sample is drawn down the device with increasing linear velocity. The particles impact onto the individual stages, which in some applications are coated with silicone oil. Any particles (generally very few), not trapped by the plates, are removed by the back-up filter to protect the pump. After sampling, the stages are separated and the active ingredients removed for analysis, (generally by HPLC [see Chapter7 of this teaching and learning programme]) following solvent washing.

Sampling of gases, vapours and aerosols - reflection

- Much analysis within this category is carried out for environmental purposes both for atmospheric air quality monitoring and for workspace monitoring;
- We have to assume that the matrices being sampled are homogeneous at the **point and time** the sample is taken;
- Where possible, gases & vapours etc. should be analysed simultaneously with the taking of the sample so as to avoid problems associated with the storage of large volumes of gases. This also has the advantage of providing **real-time analytical data**;
- Many sampling methods for this category of substances involve sampling over long periods of time, thereby producing **time-weighted average** analytical data;
- Sampling methods can be categorised as either '**grab**' or '**continuous**';
- Continuous sampling methods may be carried out using 'active' or 'passive' modes;
- Sampling for particulate matter present in the atmosphere form an important part of this category of substances;
- Many devices are available for the measurement of gases, VOCs and particulates, in order to measure an individual's exposure to toxic substances during a normal working day or shift.

Question 2.1 The terms ‘Integrity’ and ‘Representative Sample’ occur regularly in sampling terminology. Explain why they are of fundamental importance in any sampling strategy. What is the relationship between ‘Sampling Unit’, Increment’ and ‘Composite Sample’?

Question 2.2 Distinguish between ‘Static’ and ‘Dynamic’ sampling situations and describe equipment for the taking of samples of both solids and liquids, from both types of sampling situation. Give one example of each – four in total.

Question 2.3 Define the term ‘Comminution’ and explain how it could apply to samples of metal ore taken from a large consignment. The sample having been comminuted, is to be sub-sampled, prior to being submitted for analysis. Describe two popular ways in which this sub-sampling could be achieved.

Question 2.4 Distinguish between analyses giving ‘Real-time data’ and ‘Time-weighted average data’. Explain how these analysis systems relate to the sampling and subsequent analysis of gases and vapours of environmental importance. Discuss specific problems that present themselves when sampling and analysing gaseous substances.

Question 2.5 Samples of gases maybe trapped for analysis at a later date using aDsorption and aBsorption mechanisms. Distinguish between these two processes in a sampling context. An atmospheric sample containing H_2S is bubbled through a Dreschel bottle containing a solution of a buffered lead salt. Following sampling, the precipitated lead sulphide is filtered and weighed. Use the following data to calculate the concentration of H_2S in the atmosphere in mg/m^3:

Flow rate of sample 250 cm^3/min;
Sampling time 45 min;
Weight of PbS 0.0145 g

Question 2.6 Describe how a ‘Cascade Impactor’ samples air and aerosols, and explain how they have been adapted to the sampling of pharmaceutical inhalers.

Outline answer to question number 2.1

The answer to this question may be found in slides 4 - 10

It must be recognised from the outset that sampling is the most important stage in the analytical process. Analysis of a sample that is not representative of the bulk from which it was taken (and which it is meant to represent), not only will the result be meaningless, but decisions taken at a later stage may also prove very costly to the manufacturer or any other person who submitted the sample for analysis. For instance, molten steel should be sampled and preferably analysed while it is still in the furnace, so that any discrepancies in composition can be rectified before the steel is rolled out and allowed to cool. If the sample taken does not truly represent the molten steel in the pot, then the finished steel will not be of the correct composition for the purpose intended and may have to be recycled, a costly and wasteful process.

In many cases the sample taken has to be stored for several days before analysis can be carried out. It is important to ensure that the sample remains in the same state and be of the same composition, as when it was taken. This process is termed maintaining the sample's integrity.

A sampling unit is a separately identified part of an overall consignment. The sample or samples removed from that sampling unit are termed increments. These increments may be analysed separately, but with a large consignment are likely to be combined to produce a composite sample.

Outline answer to question number 2.2

The answer to this question may be found on slides 14 – 20, 37, 45 - 48

Static sampling refers to a situation where the composition of the sample remains the same over a small time interval.

Dynamic sampling refers to the sampling of a product in motion (ie flowing). The examples given in Element 1 relating to solids and liquids are respectively the sampling of grain contained in a silo and sampling from a conveyor belt, to illustrate solid sampling situations and the sampling of liquids flowing in defined boundaries to illustrate liquid sampling situations.

Examples of equipment that can be used to collect samples could include:

For sampling of solids, scoops [figures (1.8) and (1.30)] could be used, or for cross sectional sampling, devices as typified in figure (1.9) or (1.10) could be used. These devices would be satisfactory for static sampling situations, but only the scoops could be used for dynamic sampling.

For the sampling of liquids, a number of devices have been developed to satisfy particular sampling situations. These have been illustrated as figures (1.13), (1.15). For the sampling of rivers, open glass vessels, such as beakers or bottles are generally used.

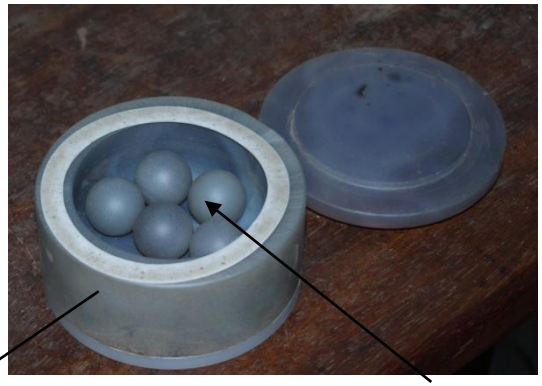
Remember, that to avoid contamination of the sample, all equipment must be clean and once the sample has been taken, it must be stored in a sealed container.

Outline answer to question number 2.3

The answer to this question may be found on slides 21 - 24

The term comminution refers to the general processes used for particle size reduction and Includes crushing, grinding and pulverising.

A large consignment of a metallic ore would need to be sampled and analysed for target metal content, as the price paid for the ore may well relate to its metallic content. The sample taken would inevitably be a mixture of particle sizes from large lumps to dust and these would need to be comminuted and sub-sampled before a representative portion could be sent to the laboratory for analysis. This would generally be achieved by the use of a roller mill followed by coning and quartering or riffling (see slides 44 & 45), dependent upon the mix and size of the resultant particles. The resultant sub-sample would then be comminuted again to reduce the particle size to that suitable for analysis. A laboratory ball mill of the type illustrated on the left could be used for this purpose.



Sample placed in the agate mill together with agate balls. The lid is then placed on top of the mill and the whole is transferred to the shaker

Outline answer to question number 2.4

The answer to this question may be found on slides 56 - 69

Real-time sampling and analysis refers to any sampling system where the sample is taken and passed directly to provide immediate analytical results. Spectroscopic instruments such as the IR gas analyser shown in figure (1.43) and the more simple 'Draeger' type sampling and analysis devises all produce real-time measurements. Time-weighted average data is obtained when the sampling system collects the sample over a long period of time for analysis at a later date. The analysis result obtained needs to be divided by the quantity of sample collected to give an average value of concentration. Sampling devices such as those illustrated in figures (150 – 1.55) will all produce time-weighted average data.

Many environmentally polluting gases and vapours are monitored continuously using both real-time methods and some passive sampling techniques. Examples of real-time analyses are CO, SO_2 and NOX (mixed oxides of nitrogen). Passive sampling devices are frequently employed to monitor an individual's exposure to VOCs or other noxious substances during a working day or shift. The sampling tube as illustrated in figures (1.54 & 1.57) can be attached to a laboratory coat or working overalls and is positioned as close as possible to the operative's breathing zone, so as to capture a sample of the same atmosphere being breathed by that operative. At the end of the working day or shift the sampling device is analysed for target analytes.

The main problem associated with the sampling of gases is the storage, hence the importance of real-time measurement. Changes in temperature, as well as diffusion through container walls can both affect the sample's integrity and thus the reliability of the analysis data.

Outline answer to question number 2.5

The answer to this question may be found on slides 63 - 69

Target gaseous analytes, maybe trapped onto solid supports (for instance activated charcoal, Tenax – a polymeric substrate) by the process of ABSORPTION. They will then be desorbed for analysis using either solution desorption (from activated charcoal) or thermal desorption (from Tenax). Using apparatus, such as that illustrated in figures (1.50 & 1.51), the target analytes are ABSORBED into the solution, generally *via* a chemical reagent with which the target analyte reacts.

The equation for the reaction is: $Pb^{2+} + H_2S \rightarrow PbS\downarrow$

Total volume of air sampled was: $250 \times 45\ cm^3 = 11.25\ l = 0.01125\ m^3$

The weight of PbS collected was 0.0145 g = 14.5 mg

The molar mass of PbS is 239 and that of H_2S is 34

Thus 14.5 mg of PbS is equivalent to 14.5 X (34/239) mg of H_2S = 2.06 mg H_2S

Thus concentration of H_2S in the air sampled was: $2.06/0.01125\ mg/m^3$

= **$183\ mg/m^3$**

Outline answer to question number 2.6

The answer to this question may be found on slides 74 - 77

Air at a constant rate, is drawn through the cascade impactor, which is a series of demountable plates generally coated in an inert viscous oil (eg: petroleum jelly). The advantage offered by cascade impactors over other methods for the sampling of particulates, is that it allows the particulate matter to the fractionated in particle size bands. Thus it becomes possible to identify the quantity of the most dangerous particles that are able to get deep into the lungs and cause lung damage.

The particles adhere to the plate surfaces when they have sufficient momentum (a combination of mass and speed of movement). The size of the flow holes diminish from the top to the bottom of the impactor, causing the smaller particles to increase their momentum, until even the smallest particles have sufficient momentum to be captured. [see figure (1.62)] by one of the plates. Following sampling, the plates are separated for measurement of particle numbers.

The process has been adapted for the analysis of the active ingredient in pharmaceutical Inhalers. The inhaler is shaken and fired into the impactor and drawn through the device by a pumped flow of air. The various particle sizes that make up the aerosol are then separated so that the effectiveness of the product can be accurately measured. [see figure (1.64)]. Following sampling, the plates are separated and the active ingredient solvent extracted for analysis by hplc.