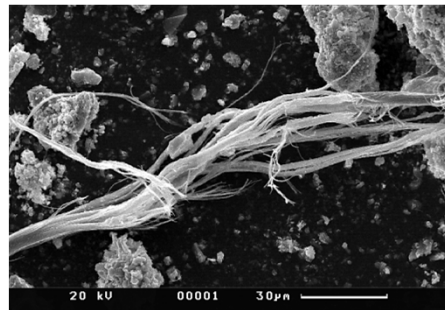
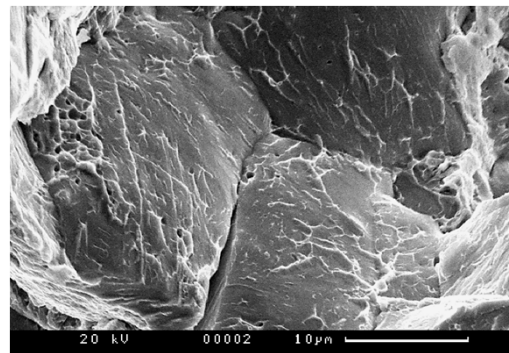


The Importance of Analysis and Appreciation of Error



Why is Analytical Science so Important?

Analytical Science truly is an inter-disciplinary science, being essential not only in Chemistry, but in the Bio-sciences, Geo-sciences Environmental and Forensic Sciences, Agriculture, Medicine as well as Engineering and Manufacturing Technologies. It is the means by which measurements (both qualitative and quantitative) are made. It is essential that the data obtained is accurate, so that the decisions made which are based upon that data are correct and appropriate.

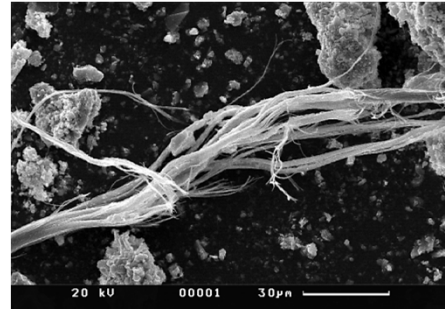




Chemical plant



Agriculture
e.g. Pesticide
residue analysis



Health & safety
-identification of
fibres



Environmental
monitoring of
effluent

Explanation of the images

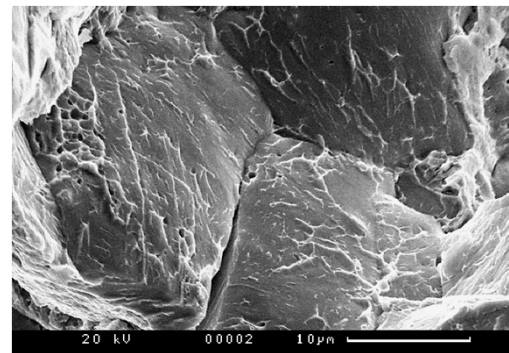
Forensic
science



Analysis of foods



Materials science



Pharmaceutical
analysis



Appreciating, Managing and Understanding Error

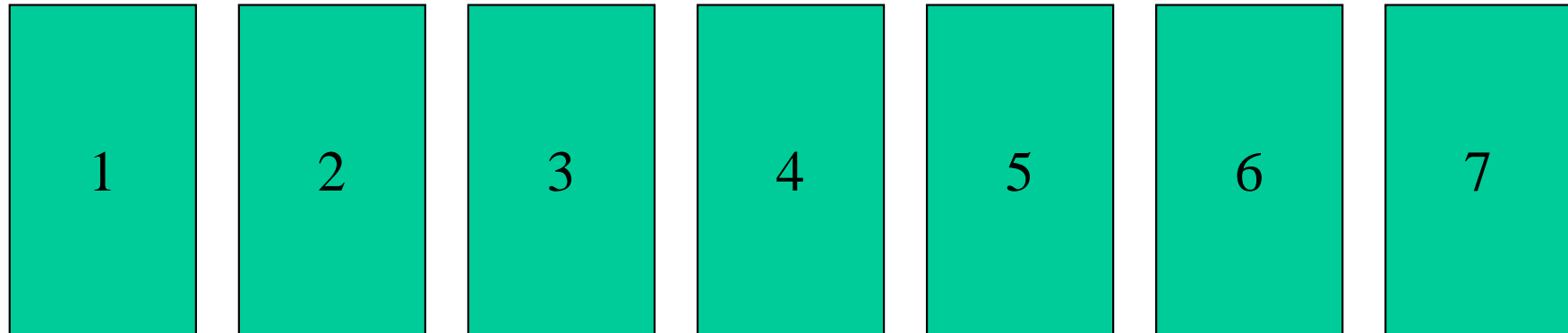


The image on the left shows a police speed camera. How accurate is the speed measured and recorded by the camera? Also, how accurate is the speedometer of the car caught speeding? To allow for both of these unknowns, motorists are rarely prosecuted for speeds not in excess of 10% of the road limit. Thus, an allowance is being made for the potential inaccuracy of the data.

All analytical data has a measure of inaccuracy and it up to the Analytical Scientist to be aware of this and to be able to express this, if necessary, in quantitative terms. **Measurements produced within a Quality Assured environment are more likely to be accurate and reliable than those produced from laboratories operating outside the principles of quality assurance.**

The Analytical Process

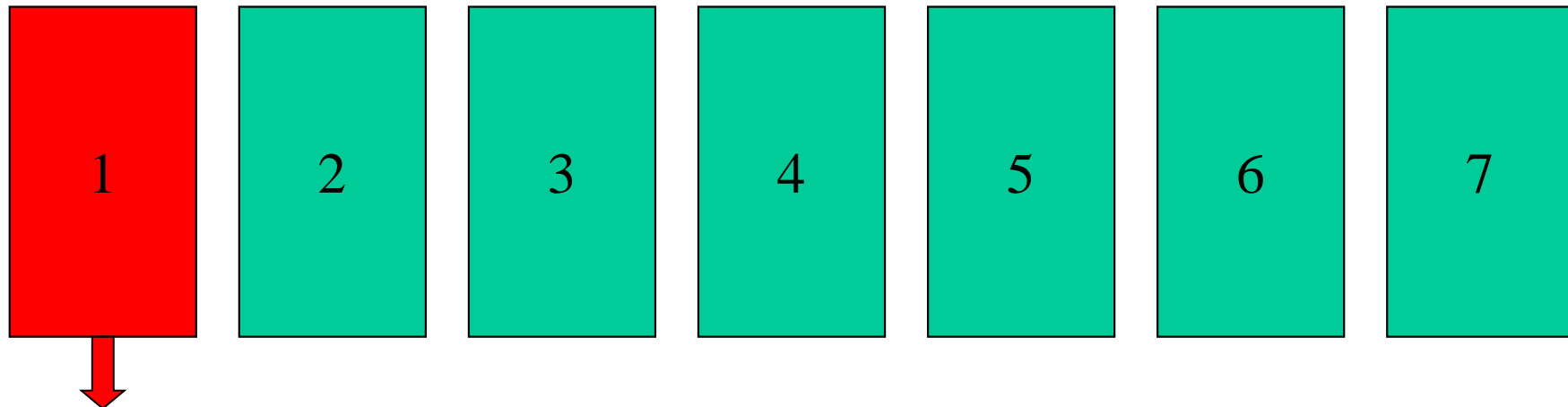
Consists of seven unit processes



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

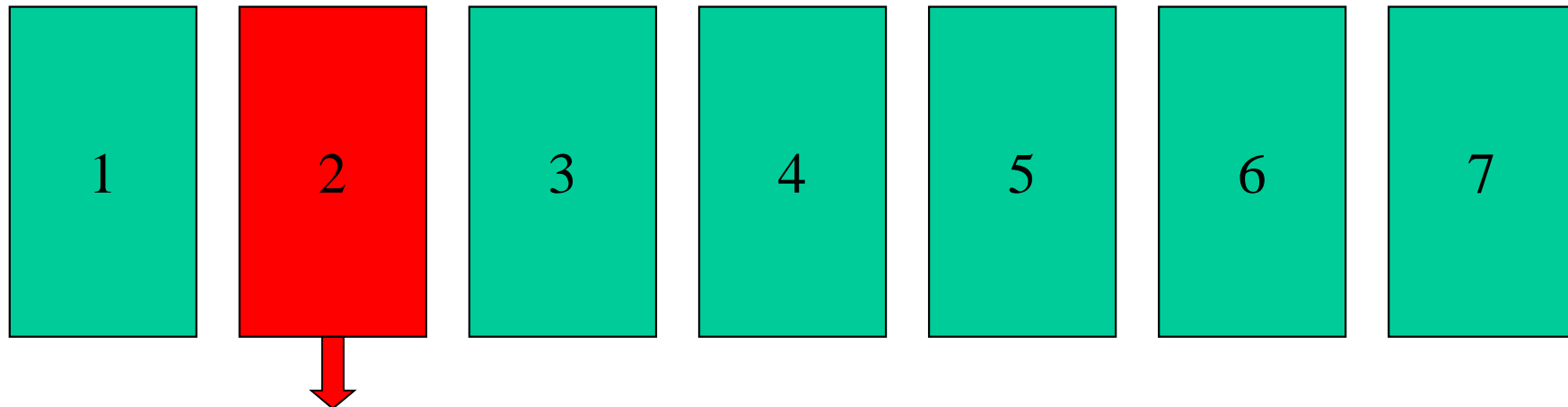
Now you can look at these in a little more detail.

Consider the problem and decide on the objectives



- Analyses cost money and should only be carried out for a specific reason
- The Analytical Scientist in conjunction with the client or sample provider, need to agree the overall objectives for the analysis
- The Analytical Scientist will often be proactive by designing analysis systems which may help to improve the quality of a product and/or reduce the cost of production.

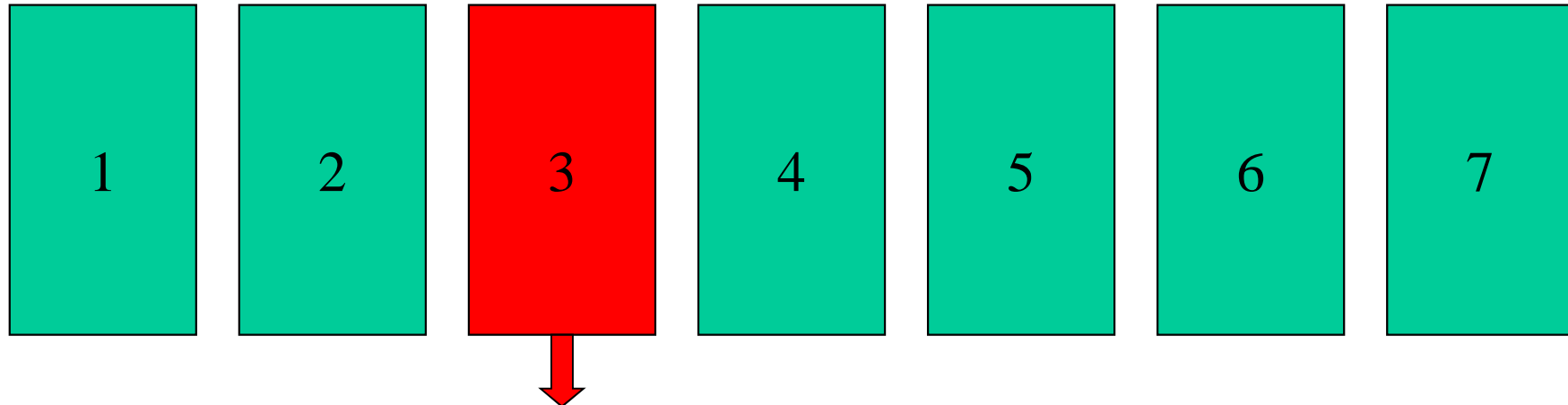
Select procedure to achieve objectives



- The Analytical Scientist can use many technologies to provide analytical information to achieve the objectives. The choice should focus on:
 - expected level(s) of analyte(s)
 - precision and accuracy required
 - sample matrix and likely interferences
 - number of samples to be analysed

Sampling

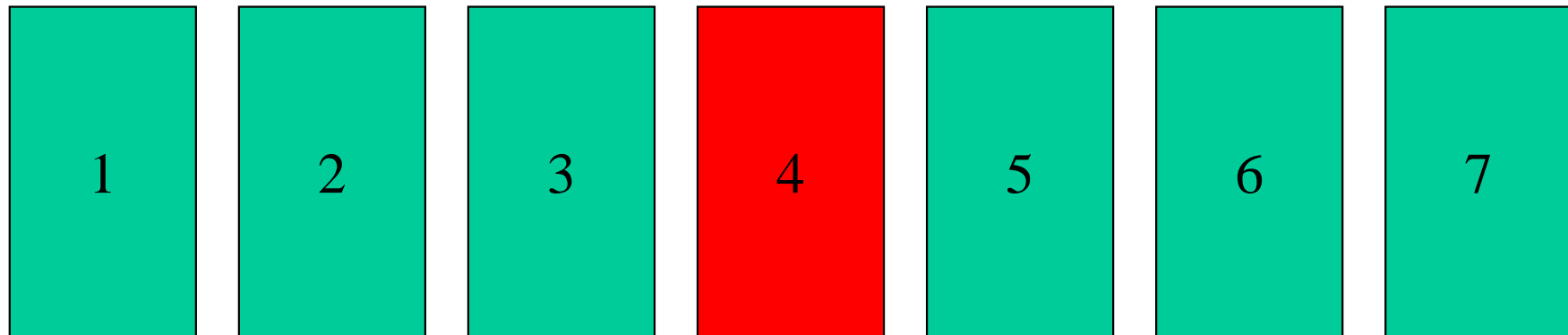
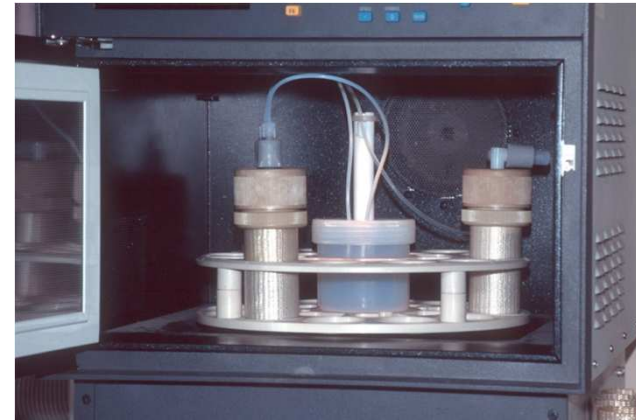
Sampling
of dried
banana
leaves



- Most important stage in the analytical process and that likely to produce the highest proportion of the total error in any analysis
- Samples where appropriate should be representative of the bulk from which they were removed
- Once the sample has been taken, it should retain its 'integrity' (not alter its structure or lose components) until the analysis has been carried out

Sample preparation

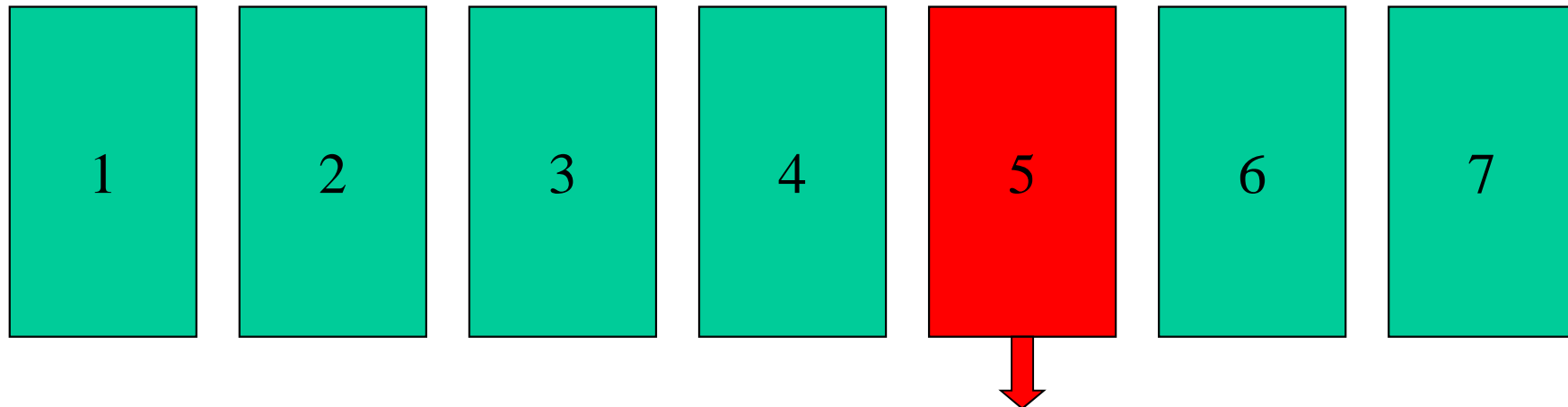
Microwave digestion oven for trace metal analysis



- Most samples requiring analysis need to be transformed physically or chemically from one form to another
- Sample preparation may involve:
 - simple dissolution in aqueous or organic solvents
 - treatment with dilute acids and bases
 - digestion with hot concentrated acids (oxidation)
 - treatment with molten fluxes at temperatures of up to 1400°C

Separation and/or concentration

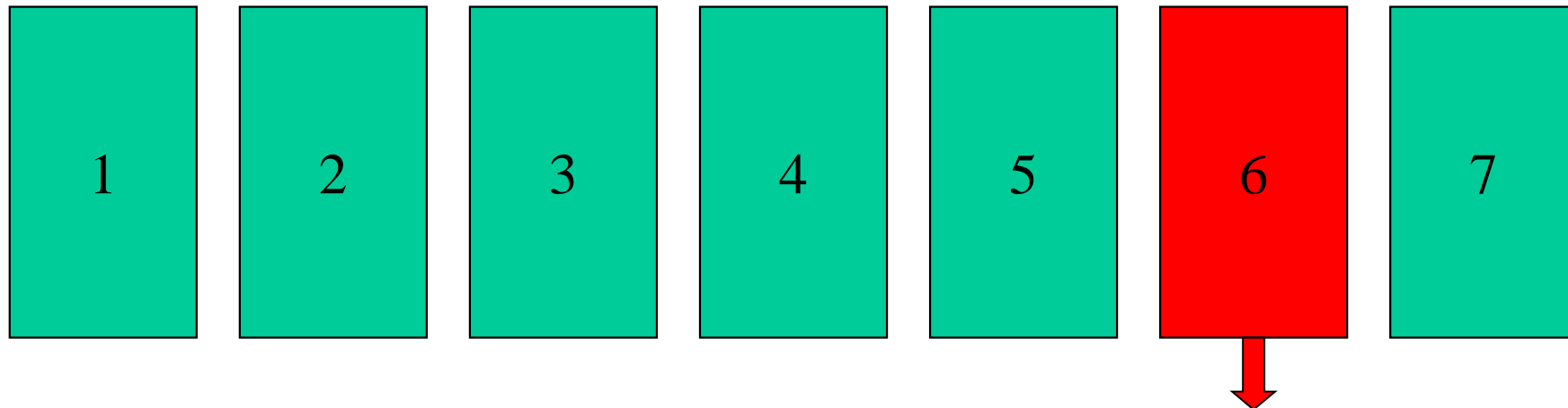
Soxflor
extraction



- Most samples for analysis are complex and could contain other components which might interfere with the final analytical measurement
- Many of the analyte levels that need to be determined are below the levels of detection of the equipment available - thus concentration is required
- The technologies used to perform both separation and concentration are frequently the same (solvent extraction, chromatography, electrophoresis etc)

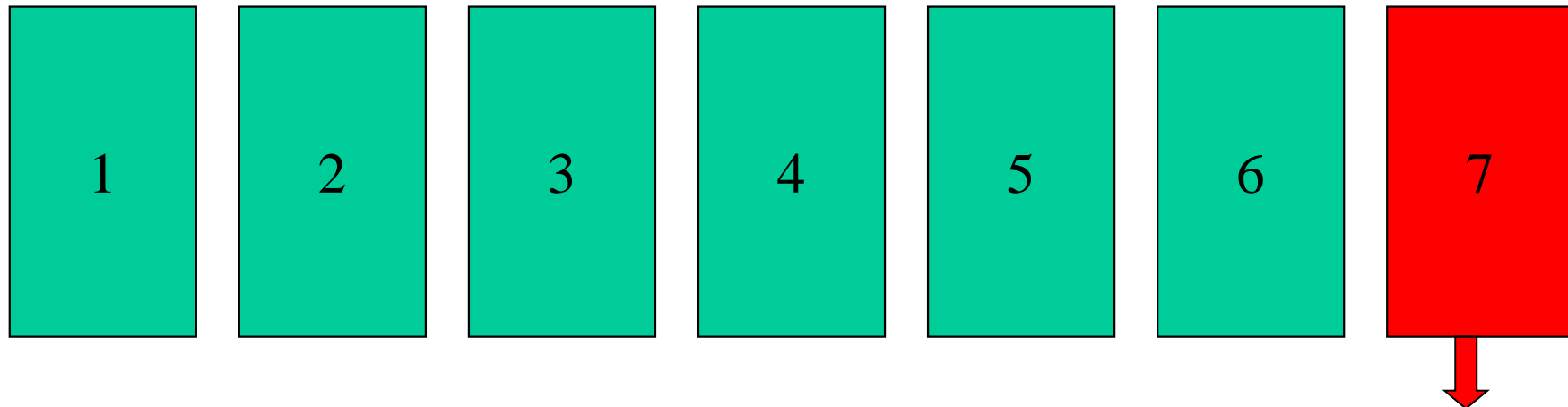
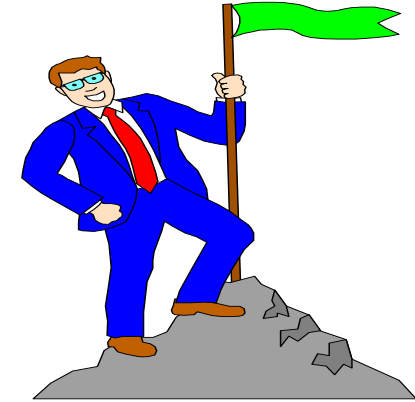
Measurement of target analytes

GC/MS spectrometer



- This is the unit process where measurement is finally made
- The technique used may be based upon either chemical or physical principles, the most important are based upon the principles of:
 - classical analysis (eg: volumetric and gravimetric analysis)
 - chromatography (eg; glc, hplc)
 - spectroscopy (eg: molecular and atomic techniques)

Evaluation of data - have the objectives been met?



- Application of statistical techniques to maximise reliability of the data
- Quantitative results to be accompanied by estimate of measurement uncertainty
- Decision as to whether or not the analysis carried out has satisfied the objectives. If not, then consider what additional tests/analyses need to be carried out



In this image, dried banana leaves are being sampled prior to analysis for total nitrogen. The leaves are first cut roughly before transferring to a 'coffee grinder' in order to obtain a representative sample.

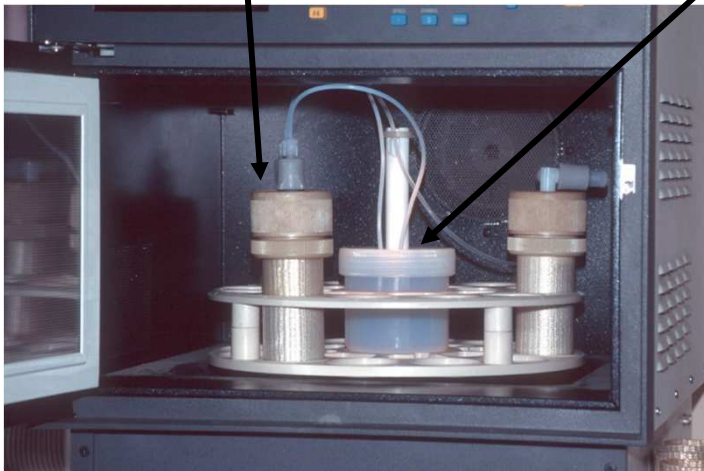
Dried banana leaves

Coffee grinder

Explanation of images

Digestion vessel

Expansion vessel to avoid explosions



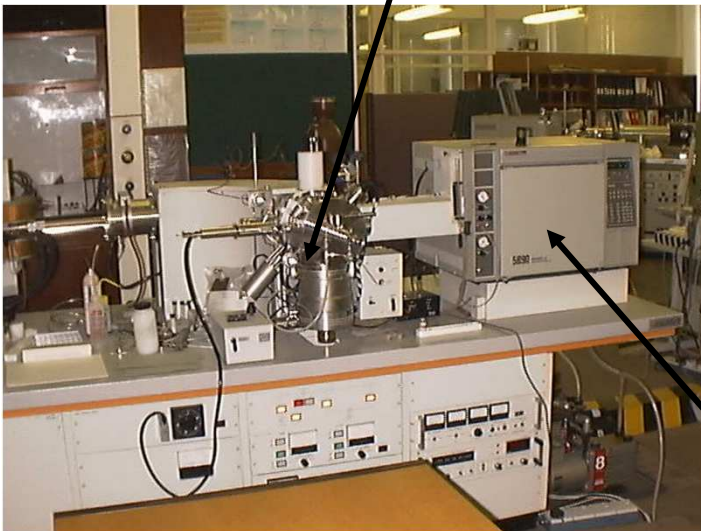
This image shows a commercial microwave oven for digesting organic matter prior to analysis for trace metallic components. The vessels contain the samples together with oxidative acids (eg. HNO_3) and the digestion occurs at high temperatures and pressures. 13



The image shows a Soxhlo extractor being used to extract oil from rape seed. This extraction method is a safer alternative to the traditional Soxhlet extraction

Explanation of images

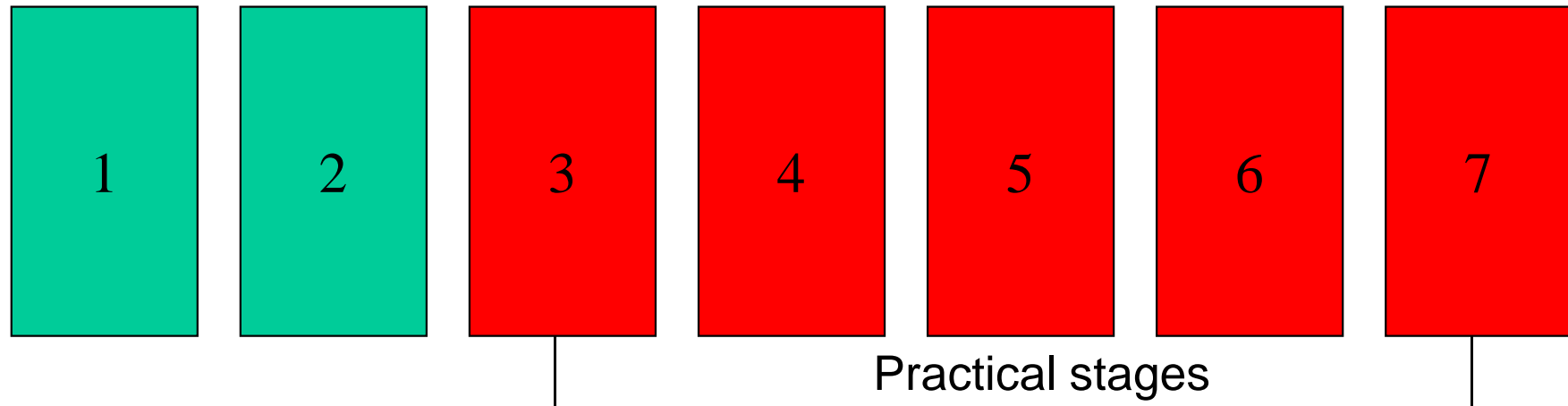
Mass spectrometer



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

Gas chromatograph

The analytical process - error components



Important to realise that error will arise in all of these practical stages in the process, with maximum error components likely to occur within the sampling (3) and the sample preparation(4) stages

Sampling - the lynchpin of the analysis

Of all of the stages in the analysis, the taking of the sample is the most important.

This is because, the sample eventually analysed will be a very small part of the bulk material to which it is assumed to relate and from which decisions of a commercial or a technological nature will be made. Samples must therefore be representative.

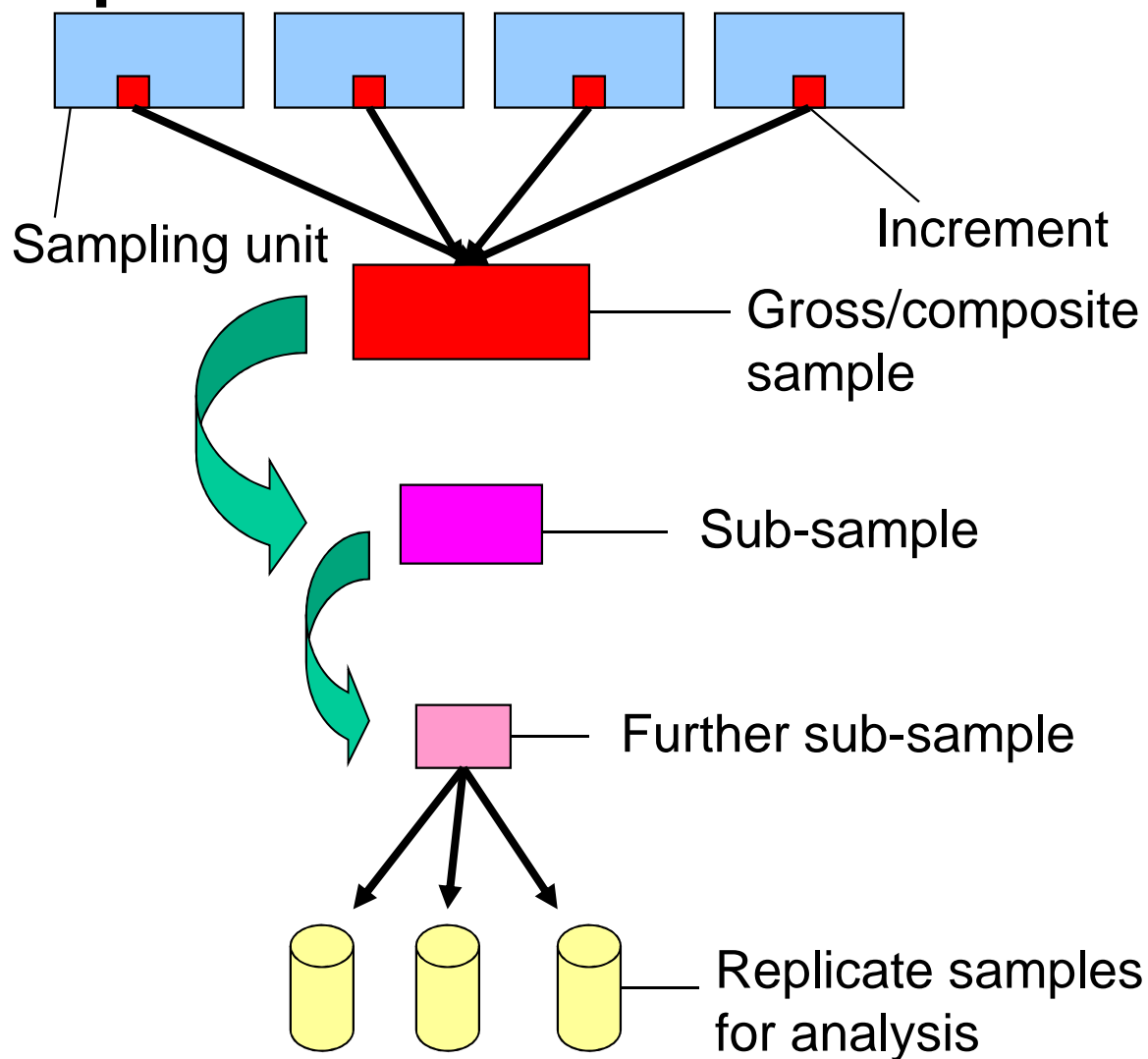
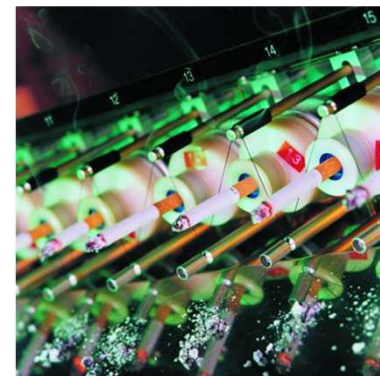
Definition of a representative sample: A portion of a material taken from a consignment and selected in such a way that it possesses all of the essential characteristics of the bulk.

EXAMPLE

Consider an Import company to which a consignment of low grade Chromium ore has been delivered. They have agreed with the supplier that they will pay for the Ore based upon its Chromium content. Samples of the Ore are taken from the consignment, but due to lax sampling practice, the samples taken are not representative. The resultant analysis gives a Chromium abundance of 5% by weight when in fact, on average, the Chromium abundance is approximately 4%. Thus the Import company pays about 25% above the value of the goods purchased.

Sampling procedures

Smoking machine to identify & quantify compounds in tobacco smoke



The diagram illustrates the situation where a **consignment** consists of a number of separate **sampling units**. **Increments** are taken from each of these units to produce a **gross sample**. This is homogenised and **sub-sampled** followed by further **sub-sampling**, finally producing **samples for analysis**. At each stage sampling must be **representative** and **at each stage further error is introduced.** 17

Sampling continued

-liquids (1)

Errors occur in sampling operations, due to the inherent heterogeneity of bulk matrices. Single phase liquids, following shaking or mixing, are likely to be homogeneous and thus a single sample should be sufficient for analysis. However, where you have a depth of liquid (eg: a drum or an ocean even), it is not possible to assume that the liquid at the top is of the same consistency as that down the column of liquid and thus a single sample is no longer suitable.



Sample is being taken away from the side of a ship to avoid metal contamination from the hull. Sample being abstracted from about 1m depth to avoid the surface layer in which insoluble organics can accumulate



Sampling continued

- liquids (2)

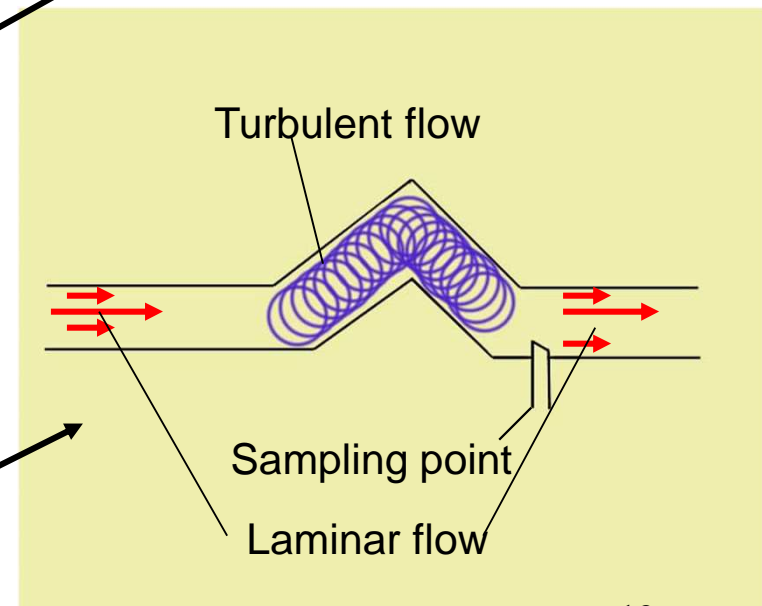
Liquids flowing in confined boundaries (eg: pipes, rivers and canals) are subject to principles of laminar flow and as such the liquid flows faster in the centre, with almost zero flow at the edge of the pipe or the bank of the river/canal.

This waterway is slow-flowing (no turbulence or mixing), samples should be taken across the width of the canal.

When sampling from pipes, turbulent flow can be created by introducing a right angled bend into the pipe, with sampling just before the flow returns to laminar conditions.



Huddersfield Narrow Canal



19

Liquid flowing in a pipe

Sampling continued - solids (1)

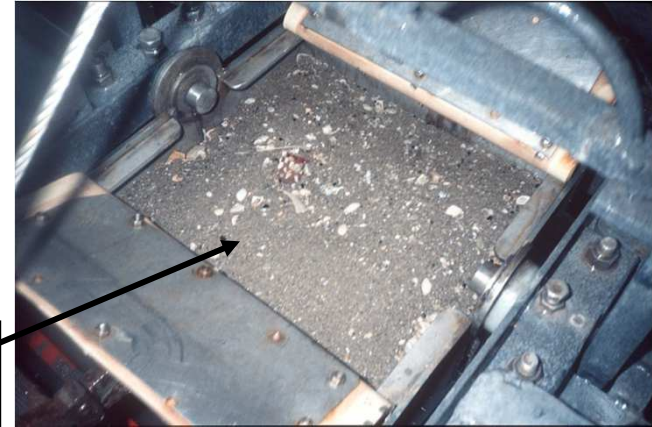
In terms of potential heterogeneity, the sampling of solid matrices poses a major problem. Following extensive grinding and mixing, solids can still exhibit some heterogeneity and thus introduce errors into any analysis. Typical examples of solid sampling situations are:

- pharmaceuticals (tablets & powders)
- minerals
- contaminated land surveys
- agricultural products (e.g: seeds, grains, leaves)



Sampling continued - solids (2)

'GRAB' Sample of sediment taken from the bottom of the North Sea. The sample is air dried before discarding any large stones etc. The remaining sample is then sub-sampled to reduce the quantity before being ground, sieved and then stored in clean containers prior to analysis



Grain silo - take samples for analysis when the silo is emptied



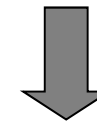
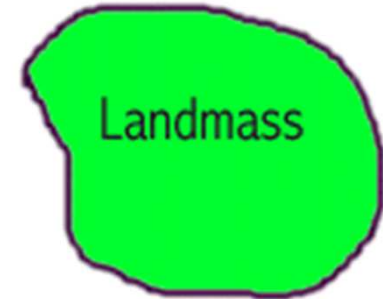
Derelict industrial site which may require a contaminated land survey prior to redevelopment dependent upon previous usage. Concrete samples taken as 'cores'



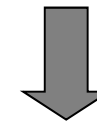
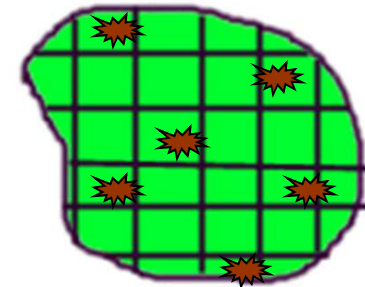
Sampling continued

- statistical sampling

Because of the inherent heterogeneity of solid matrices, the process of 'Statistical Sampling' is often employed. This is ***based on the principle that all particles or portions of the population (material to be sampled) have an equal probability of being present in the sample that is taken.*** This is best illustrated by considering the sampling of a potentially contaminated piece of land where contamination may be concentrated in small areas of the overall land mass. Given that the cost of the survey, the number of samples taken and the potential accuracy of the result are all interrelated, a compromise is normally adopted whereby the sampling sites are chosen randomly within some strict guidelines



Divided into smaller imaginary plots



Samples (★) taken from random plots or randomly from each plot.

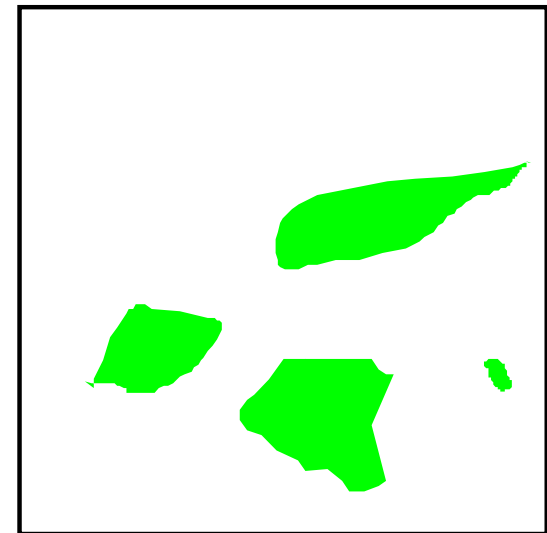


Samples combined (composited) for analysis or analysed separately²²

Sampling continued

- contaminated landfill site

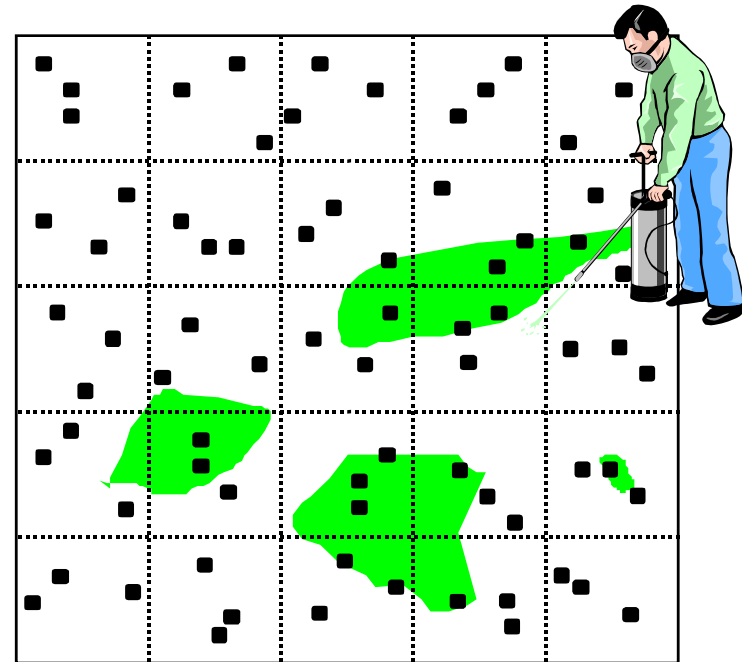
Suppose that the site is heavily polluted but in irregular patches. If you are not aware of the location of the patches but there is the need to reduce the average pollution concentration over the whole site to below 1%, **you need a sampling strategy that shows by analysis which areas require treatment and which do not.**



Target area of land fill site showing (unrevealed) patches of pollution

Contaminated landfill site (2)

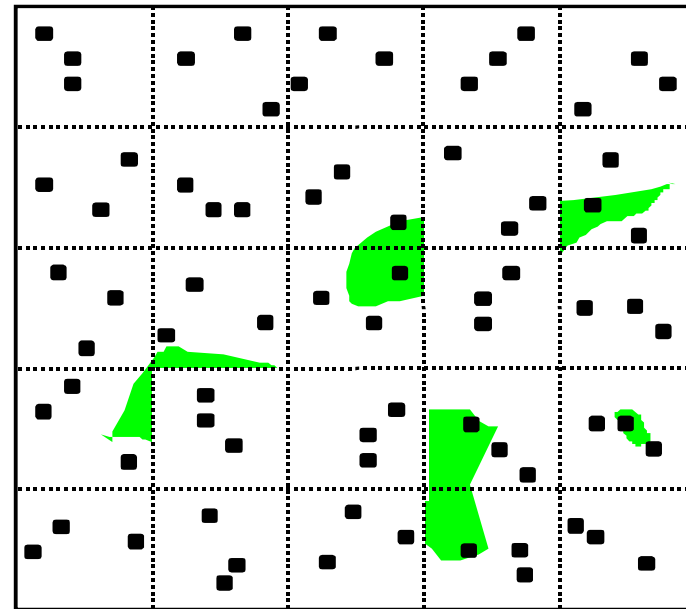
Divide the target area into a grid of sampling cells and take 3 random samples from each grid. From the analyses you can identify which of the cells are the most contaminated and treat them accordingly.



Land fill target area with 3 random sampling positions in each grid area.

Contaminated landfill site (3)

By cleaning up only those grid areas identified as having the highest pollutant abundance you can now calculate whether or not the target of less than 1% has been achieved. If it has not, then further clean up of the other areas can be carried out



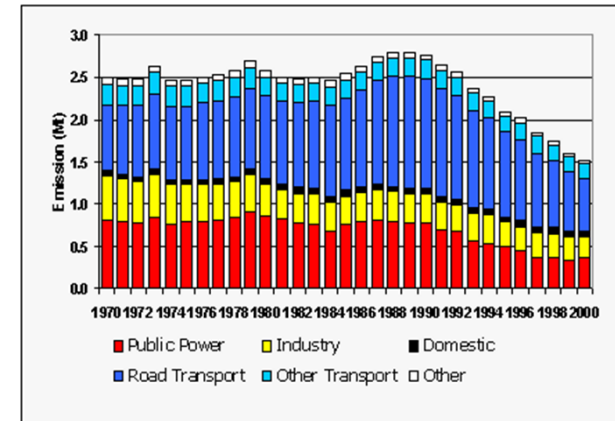
Target area of land fill site after treatment of selected grid areas

Sampling continued

- air, gases & vapours(1)

Given the difficulties of taking and storing gas samples, it is recognised that gases etc. are best analysed in situ by a suitable on-line analyser. Such analysers are routinely in use to monitor levels of CO, CO₂, SO₂ and oxides of nitrogen within the air we breathe.

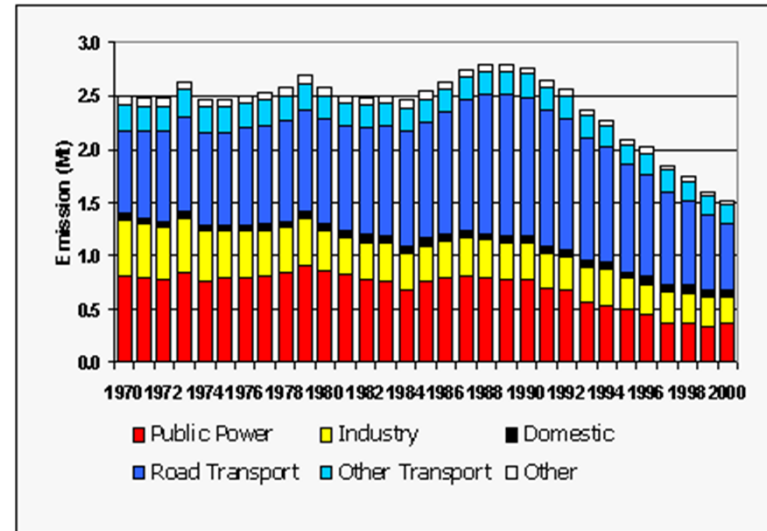
Many organic vapours can either be monitored on line (e.g by using dedicated IR analysers) or they may be trapped onto suitable substrates (e.g: activated charcoal or TENAX) for analysis in the laboratory. Given that it is impossible to tell whether or not the samples are homogeneous, time weighted average data is frequently quoted.



Sampling continued

- air, gases & vapours(2)

Data set to illustrate the reduction in NO₂ emissions in the UK between, 1970-2000. Analysis for NO₂ carried out by using either diffusion tube monitors or by chemiluminescence analysers



Simple absorption devices used trap volatile organics (VOCs) for eventual analysis in the laboratory:
diffusion tube containing Tenax
tube containing activated charcoal
cartridge containing C₁₈ adsorbant

