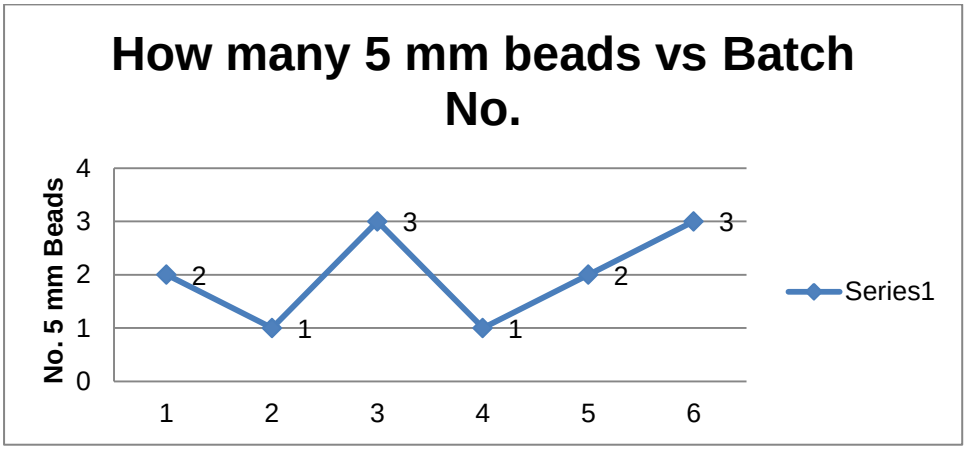
Chapter 2

It is important to note that in any sampling process, your sampling plan identifies the required health and safety measures to incorporate (as stated in chapters 1 and 2). A number of guidance documents are available and one which focuses on fieldwork is:

The BGS + NERC Safety fieldwork:
https://nerc.ukri.org/about/policy/safety/procedures/guidance-fieldwork/

Feedback to Part (a) of Problem 1

Each 10 mL volume poured from the bead mixture in the tube should in theory provide you with two 5 mm beads, if their distribution is homogeneous, together with the 2 mm beads. The mean value from sampling the whole 60 mL volume will always be the expected quantity; i.e. 12 beads / 6 batches = 2 beads / batch. However, this last calculation is based upon sampling the whole quantity of "bulk" or "source" material, which is not possible in many sampling cases. Here, it is often helpful to plot the number of 5 mm beads against the batch number to see the progression through each experiment. One possible example is shown below.



Now, it is noted that 12 x 5 mm beads are equivalent to ~188 x 2 mm beads in volume (and mass if the beads are the same material density); so in numbers present in the 60 mL total volume, we would be seeing ~ 12 x 5 mm beads and ~ 8980 x 2 mm beads after correction (based upon 64% packing occupancy – see also Chapter 8); compared with the ~9170 x 2 mm beads present in 60 mL if no 5 mm beads were added. Imagine if the material from the 12 x 5 mm beads contained our "analyte" of interest and the 2 mm beads did not. We can immediately begin to see the differences that can arise due to a calculation using population (based upon a simple number) and upon a sample's diameter (based upon volume and hence particle size; or mass if the material's density is the same throughout). If we ground down our 12 x 5mm beads to form ~188 x 2 mm spherical beads and added these to the 8980 x 2 mm beads, then only an "ideal" homogeneous distribution of these analyte beads

would follow the binomial calculations shown in detail in chapter 8 for any associated sampling to be representative. However, at this stage a simple population vs particle size basis demonstrates the importance of what we mean by a “homogeneous” distribution and where errors may be introduced when it deviates from “ideal”.

Feedback for Part (b) of Problem 1

After a certain amount of tapping of the tube, it is noted that the 10 mm beads begin to break the surface of the 2mm beads. In effect, the larger particles are “lifted” to the surface of the “sample” by the action of the smaller particles being vibrated. In time all 10 mm beads will be at the surface, under such actions, despite starting at the bottom of the tube. As a result, pouring the top 10 mL of the tube can produce anywhere between one and all five of the 10 mm beads; not a good outcome in terms of representative sampling, from a supposedly mixed sample!

This is sometimes known as the “void-filling” effect‡. The smaller particles are able to fill the gaps or voids around and between the larger particles and the smaller particles are able to pack more efficiently when vibrated. This results in slowly raising the larger particles to the surface of any newly formed strata being efficiently packed beneath.

‡ or the “Brazil Nut” effect when applied to our breakfast ‘muesli’, discussed in chapter 1 of the book

It is noted that the ‘representative sampling’ of a bulk material, comprising a broad range of different sized particles, can be compromised if “segregation” and what is also termed “stratification” effects are not taken into account. As seen in Chapter 2 (section 2.5.1), a ‘sampling thief’ allows for three dimensional effects to, at least be considered when sampling particulate materials.

Hence, such effects of “stratification” of particles by size can be seen in our everyday world; for example when over-working a particulate sample by “cone and quartering”, when dispensing materials from vibrating hoppers and silos, when acquiring samples from sacks containing multi-sized particulate materials, when transporting materials by conveyor and sometimes, even when we pour out our breakfast muesli.

Feedback on Problem 2

i) taking one sub-sample at a time and plotting the cumulative accuracy and precision as we go along up to taking the full 32 sub-samples.

Sequentially, we are taking, one sample at a time, alternating as 0.5 mg and then 1.5 mg then 0.5 mg then 1.5 mg then…..etc. These are the first ten samples as shown below.

Number of samples taken (n) cumulative	Value in mg of Cu sample taken	Cumulative Mean Value, mg [total value/n]	Recovery as a %	Cumulative Precision
1	0.5	0.5	50	
2	1.5	(0.5+1.5)/2 = 1	100	v. v poor
3	0.5	(0.5+1.5+0.5)/3 = 0.83	83	v.poor
4	1.5	4/4 = 1	100	v.poor
5	0.5	4.5/5 = 0.9	90	poor
6	1.5	6/6 = 1	100	poor
7	0.5	6.5/7 = 0.928	92.8	fair
8	1.5	8/8 = 1	100	fair
9	0.5	8.5/9 = 0.944	94.4	v. fair
10	1.5	10/10 = 1	100	v.fair
11	0.5			
12	1.5			
13	0.5			
14	1.5			
15	0.5	14.5/15 = 0.967	96.7	q. good
16	1.5			
17	0.5			
18	1.5			
19	0.5			
20	1.5	20/20 = 1	100	good
21	0.5			
22	1.5			
23	0.5			
24	1.5			
25	0.5	24.5/25 = 0.98	98	good
26	1.5			
27	0.5			
28	1.5			
29	0.5			
30	1.5	30/30 = 1	100	v.good
31	0.5	30.5/31 = 0.984	98.4	v.good
32	1.5	32/32 = 1	100	v.good

It can be seen that as we cumulatively build up our values, every second sequential sample taken (2^{nd} , 4^{th} , 6^{th} , 8^{th} …) provides us with 100% recovery. While every odd numbered sample (1^{st}, 3^{rd} , 5^{th} , 7^{th} ,….) provides us with an increasingly more accurate cumulative value with regards to that overall mean value expected (1 mg / sample cube). It starts out at only 50% but quickly focuses (after 5 samples) on being greater than 90% and improves continuously so that samples 31 and 32 are close at 98.4 and 100% respectively. The same effect is seen on the cumulative precision, starting out as very poor indeed for the first six or seven samples but improving quite quickly after 10 samples to demonstrate good to very good precision from half way through (n = 15 onwards).

Hence,

ii) taking twice as many sub-samples, two cubes each time which sit next to each other, and looking at the accuracy and precision as we go along, means that you will always have 100% recovery (because every two cubes will have [0.5 mg + 1.5 mg] of copper and hence will also produce the very highest precision, as every two cubes sampled together will present exactly the same combined copper value of 2 mg.

To summarise, these cube scenarios demonstrate that our sample's value, in terms of it being representative, depends upon how many samples we take, how much sample we take and the distribution of analyte in our bulk or source material.

Feedback on problem 3

The sampling plan should include the following - after suitable safety requirements and handling procedures are taken into account:

Quantity of drums delivered,

Content of each drum by sampling (see fig. 2.10 b and below):

Whole depth of drum is to be sampled using a glass 'sampling thief'.

Quantity in each drum from the dimensions of the drum and the depth of waste in each measured using a glass 'sampling thief'.

Gross total volume delivered is calculated using above information.

Consider possible stratification, so each drum's content visibly scrutinised using the transparent glass thief. Look for settled material at the bottom. Waste material will usually

contain residues from their use and any processing involved (in this case metal residues etc.).

Suitable volume of liquid taken from each drum – sufficient for analyses of constituents and their replicates (e.g. 200 - 300 mL+)***** Noted that drums can contain up to 208 L.

If a glass thief is used then the "thief's" dimensions will be considered in terms of length and volume. For example, a normal oil drum is approx. 850 to 900 mm in depth and so a 1 m 'thief' of ~ 20 mm bore (internal diameter) will contain ~283 mL if a 900 mm sample depth is taken.

Each sample is labelled and placed in a sealed glass bottle / vessel.

***** Simple analyses are performed using suitable instrumentation after some separation of the various constituents (see chapters 3 and 4) but to note that cutting oils can also be determined by a relatively simple titration technique.

Feedback on Problem 4

Here it is important to think in three dimensions, just as you would when sampling a solid or a diffusing gaseous bulk source. The degree of heterogeneity is dependent upon the efficiency of mixing and for such a large tank, stratification and pockets of variation will decrease as the efficiency of mixing increases. While efficient stirring is expected for both quality and financial reasons, this effect may be tested in this sampling step, if required. Therefore the use of a suitable pre-cleaned and rinsed (with the sucrose solution itself just prior to sampling) plastic 'sampling' apparatus which allows increments to be acquired from not just the surface but also the middle section and down the full depth of the tank (see section 2.5.2 and figure 2.10) would be a requirement. While some large tanks are actually designed to allow stratified sampling directly of the contents (built-in to the tank), not all have this facility and ease of sampling will also depend upon the viscosity of the material being prepared. One would also have to consider the cross-sectional area of the tank, to sample from above, in order to allow a more representative sampling regime to be undertaken.

In order to avoid cross contamination of the entire tank contents, one approach may be to use a suitable length of a pre-cleaned and rinsed plastic tubing that can be lowered to various depths from the surface (e.g. 30 cm, 5 m and 9.7 m) and the contents from that depth, pumped to a pre-cleaned and rinsed vessel (glass or plastic) of suitable size (usually 100 to 500 mL. The volume of liquid already in the pipe will first need to be flushed through / discarded, every time a new sampling point is chosen, to allow a representative sample at that depth to be acquired. The principle shown in Figure 2.10 (c) in chapter 2 may be used to collect the sample.

Taking a series of individual samples, say x 9; three depths at each of three positions around the tank, in this manner will provide not only a mean measure of the sucrose concentration with its uncertainty but also allow separate information to be obtained on the stirring

efficiency value if required. Of course, composite samples from this will provide a 'mean value' but will also be reduced in terms of its confidence and spatial information (distribution) will be lost.

Feedback to Problem 5, the detection of hot spots and numbers of samples.

The constant, 0.59, in equation 2.1 of Chapter 2 is based upon p = 0.05 (95% CL) and a circular shape factor 'S' = 1.0.

If the diameter of the hot spot is 10 metres then the radius, R, is 5 metres. The grid size is therefore:

$$G = 5 / 0.59 = 8.5 \text{ metres.}$$

The number of sampling points in the 0.4 hectare site (4000 m^2) is therefore:

$$n = 0.4 \times 10^4 / (8.5)^2 = \sim 56 \text{ (between 55 and 56)}$$

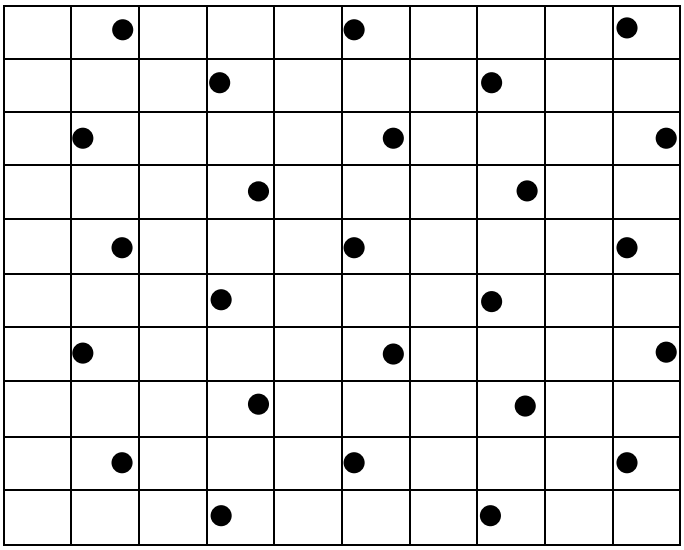
The number of sampling points is a whole number; i.e. 56 and the grid size of the sampling pattern should be 8.5 metres (sampling points = 8.5 metres apart). Using this sampling regime, we will be able to locate where the "hot spot" is.

However, this will in theory pick up at least one and at most two samples (at the 95% CL) within the 10 m diameter "hot spot" and provides no further information on the distribution / layout of the "hot spot" in relation to that one or two sample(s). The question asks for identification of the "hot spot" boundary.

To identify the "hot spot" boundary to a greater level of confidence, you would need to produce a new grid based around the sample(s) where the hot spot was found. If you assume that the one or two samples can be at any point within the 'hot spot' then the worst case would be that it was (or they were) identified at any point on the circumference of the hot spot. As the grid system calculated was based upon 8.5 m spacing, then in two dimensions, the four grids around the sample(s) will be a square that encloses the entire hot spot and some of the uncontaminated land.

We can construct another grid pattern within this identified area but now based upon a systematic approach, in order to find the boundary of the hot spot. If we construct our square, 2 x 8.5 m by 2 x 8.5 m (17 m x 17 m), we can perform the sampling again but as stated based upon a systematic sampling regime as outlined in fig 2.3 of Chapter 2. It should be

possible to adopt either a 5 x 5 systematic, aligned grid with random start or a 5 x 5 systematic herringbone design, unaligned with a random start (see below diagram). This makes the new grid arrangement ~ 3.4 metres apart (25 sampling points for analysis within the 17 x 17 m area), allowing the boundary to be identified within approx. ± 1 metre or less when sampled and analysed.



In effect, the overall approach taken above is one of stratified sampling. By using the "hot spot" approach first to indicate where the hot spot actually is, within the 4000 m^2 area and to then use a systematic grid approach within the indicated (selected) area to identify where the actual boundary of the circular hot spot lies.

It is also sobering to reveal that, in order to achieve the same result just from a "hot spot approach alone, in one sampling grid system based upon a sampling scheme that would pick up our hot spot boundary to within ± 1 meters, you would need:

Diameter of hot spot = 2 m (based upon approx. ± 1 meter accuracy),

Therefore the radius = 1.0 m,

Our grid system would then be based upon G = 1.0 **/** 0.59 = 1.69 m

And our number of samples, n, would be: n = 4000 **/** $(1.69)^2$ = ~1400 samples

Rather than the 81 (56 + 25) samples we arrive at, when using a stratified approach. Just a thought!

Feedback on Problem 6

Two requirements are asked for and both depend upon a particular level of confidence with their sampling.

i) For the first requirement, it is a logical expectation that ALL packaging (100%) will meet quality control, all properly sealed and with no damage to the packaging; in this case, all 8 tablets sealed within their "blister packs". Therefore, if 100,000 packs are produced, a suitable system should be in place that checks all 100,000 and identifies any light (< 8 tablets) packs, or damaged / improperly sealed tablets / packs exiting the pack sealer, prior to being boxed. This is normally an automated system and ensures that the probability of a member of the public buying a box containing damaged or low quality goods is statistically so low as to be 'a value within the "noise" of the process'.

ii) For the second requirement, we need to ensure that the contents of the packs with their tablets are, at least the labelled content value and that the statistical likelihood of that value being below this labelled quantity is very low. There is also the requirement that the content of our pharmaceutical drug within the tablet is within a statistical value (± range) to ensure not too much is present. For a sufficiently large bulk sample number, n (in this case 100,000 packets produced), we can to a first approximation assume a 'normal' distribution around the lower limiting value expected from our labelling. Our pilot plant will be set up to produce "pills" of the "correct" formulation and finely tuned to ensure the required quantity of active drug in each tablet has a mean value just above the labelled value (e.g. labelled mean values of 500 mg for Paracetamol and 200 mg for Ibuprofen, etc.). The distribution of values around that mean will be controlled by the production system to be as narrow as possible (precision of the production) so values fall within a tuned concentration range. We know that around 95% of this distribution's probability lies within 2 standard deviations of the mean value. We can therefore estimate (based upon this confidence) our first number of samples to take. It is important to note that our confidence interval is a statistical estimate based upon the observed data from the production run.
For example, if our series of preliminary, smaller pilot runs prior to this larger, full scale production run all showed (from 10 analysed samples each) that the mean value of active drug in the tablets is 510 mg but with a standard deviation of 10.2 mg (a % RSD of 2.0) then, if we sampled 100 packets at various stages of this larger production and then measured one tablet out of every sample packet, we could then calculate the new mean and standard deviation values and compare these to the previous estimates to gauge inter-production control. The 100 packets would be sampled from throughout the run but on a random basis or preferably random within a stratified basis; not a systematic basis. This approach is undertaken to reduce errors associated with sampling frequency which may be part of a production process. A stratified random basis would allow the whole

production run to be sampled. It is of note that the initial tablets formed from a batch may well be discarded until the production process settles down and the rest would go on to be packed. It may be that, as the control chemist, you are part of that 'identification through measurement' process team.
The data obtained can be used to produce a graphical distribution around the mean value for further statistical analysis, including measurements of confidence interval at a selected confidence level and subsequent estimates of the statistical probability of a tablet containing above or below certain limits of the drug. As an example, based upon the above values, we might expect the 100 samples to produce a sample mean of similar value, ~ 510 mg and an improved value for our SD; for example this might now be ~ 5 mg and therefore at the 95% confidence level, a confidence interval of 509 to 511 mg for the population mean (actually 510 ± 0.98 mg). To calculate the actual number of samples to take will be dependent upon the sampling statistics associated with this specific production system and upon defining the error that is acceptable (as a relative standard deviation). See Chapter 8, Section 8.3 and the on-line additions for Chapter 8 to see an example of this sort of calculation.

Feedback to problem 7

i) They are all acidic gases

ii) It should be possible to take advantage of their chemical and physical properties, i.e. acidic in reactivity and also gaseous in physical state, in order to trap them (see Section 2.5.3.). Sampling the gas 'stream' using an inert tubing material with a pump that is set at a known fixed gas flow rate and trapping the gases using; a) a Drechsel bottle containing a solution that reacts with acids (e.g. alkaline solution such as $NaOH_{(sol)}$ for gases like CO_2 and H_2S, or $Na_2CO_{3\,(sol)}$ for gases more acidic than CO_2); or b) a solid 'absorber' that not only traps the gas but also can release the gas from the solid at a later stage by heating, or washing with a reactant etc.; or c) Use gas bags to collect the evolved gases (either 'pump-in' or 'draw through') and sub-sample from these using a gas syringe‡. The position of the sampler tube for collecting the gaseous emissions is important and spatially critical for three of the five scenarios on site ($H_2S_{\,(g)}$, $SO_{2\,(g)}$ and $HCl_{\,(g)}$). Their positioning will be dependent upon the requirements of the analysis and agreed from discussions (through asking of questions and defining the object of the analysis). For example, the emission of $SO_{2\,(g)}$ from a power station will be linked to atmospheric emissions monitored by the Environment Agency (EA) and would normally be sampled within the final emission stack venting to atmosphere. The emission of $H_2S_{\,(g)}$ from a Landfill Waste Facility (TLV and safety levels) would normally be monitored from the capped landfill gas pipes which channel methane and other gaseous products from the main site. Again these will be linked to any possible atmospheric emissions monitored by the Environment Agency (EA). The

levels of $HCl_{(g)}$ emitted from an electrolysis-based precious metal plating bath would need to be monitored, particularly for the health and safety of those on site (Health and Safety Executive [HSE] guidance on exposure / sampling: http://www.hse.gov.uk/pubns/guidance/ocm6.pdf) and these samplers would be focussed above and around the bath itself, as well as further afield in the working environment. Such a bath would have a fume hood or similar air-drawing system, to control the air around it.

The collection of $NO_{2\ (g)}$ from the car engine can be directly from the engine's exhaust manifold or the car's exhaust pipe (as in vehicle MOT requirements).

The $CO_{2\ (g)}$ present in carbonated water is, however, already captive when sealed in a packed bottle. While the water itself will "acquire" a certain amount of $CO_{2\ (g)}$ under pressure (between 2 and 3 atmospheres and monitored by a pressure gauge) when supplied from a pressure vessel to the packed bottle, the final quantity or concentration in the bottle is the most important measure (usually around ~ 8 g / L at room temperature) , due to various losses. Hence, sampling to some extent is already pre-packaged. The total $CO_{2\ (g)}$ in each bottle, when measured by a selective technique will contribute to the collective mean value calculated from the number of bottles sampled. It is noted that solubility and reactivity of $CO_{2\ (g)}$ is dependent upon pH and temperature.

However, it is noted that these days, real-time monitoring is possible using "gas sensors" which if calibrated and maintained, can provide continuous qualitative and quantitative measurements remotely. All the example gases above have a health and safety issue, whether they be an asphyxiant (like CO_2), or generally poisonous due to their chemical reactivity (like SO_2 and HCl) or highly poisonous due to their biochemical activity (like H_2S and NO_2).

‡ The reader is directed to the "Health and Safety Executive" Methods for the Determination of Hazardous Substances (MDHS 70) **General methods for sampling airborne gases and vapours.**