Exercises and Short Problems: Solutions

1. A "homogeneous sample" is one for which there is no evidence of variation throughout its extent, with respect to the property being measured.

   Demonstrated by e.g. Na^+ ions in a drinking water sample or nitrate ions in a river water sample, or Argon levels in an air sample, [even an analyte in a standard calibrant solution] etc.

   A "random sample" is one that is chosen from the bulk material on a random basis; where random relates to being non-selective and unbiased.

   An example is where a large field is divided into 100 equally sized plots, numbered sequentially 1 to 100 and then 10 samples are acquired from this field using a random number indicator programme to select the 10 plots.

2. Consider whether element specific or selective, molecular selective or (possibly) specific, sensitivity of instrument and concentration range covered, any separation requirements (chromatography), the phase of the prepared sample (solid, liquid or gas – volatility etc.) and state of the analyte of interest, possible interferences with a particular technique, etc. etc. Give as much detail as you can to the reasons for selecting the technique.

   a. ICP-AES is most obvious on sample's digestion solution as it is an element-specific technique. A possible but not easy measurement by UV-vis Spec. after digestion and either selective Mn-complex using suitable reagent or oxidant to permanganate. Iron is one major interferent and needs masking. Some discussion of details for latter technique required to allow this measurement. ICP-MS is too sensitive (too great a dilution required) and doesn't handle digestion solutions at high concentration well.
   b. ISE [Fluoride] directly after digestion/extraction and total ionic strength buffer adjustment. Some anions may interfere but if F^- concentration is high compared with the other anions then may be compensated. UV-vis spec. is possible with suitable fluoride chemistry to produce a suitable fluorine-absorber species. While ion HPLC could separate anions like F^-, UV-vis not directly possible unless suitable post-column reaction chemistry is demonstrated, as shown by above.
   c. GC-MS or HPLC-UV-Vis detection - requires separation of "individual" PCB components that are in the soil. Extraction from soil using suitable organic extractant prior to adjustment and then measurement. Molecular fluorescence on its own would not allow individual measurement.
   d. ICP-MS or Atomic Fluorescence would allow the particularly low levels of total Se in vegetables to be measured after suitable digestion / extraction technique has been employed. The AF technique would require a H_2Se volatile species to be produced, for introduction to the AF cell system but both techniques demonstrate good element specificity. The lower levels of transition elements in vegetables should not cause too great an interference in the AF technique.
   e. Molecular Fluorescence is one possible route, but care should be taken. Total quinine (Quinine, Quinidine etc.) levels after suitable extraction technique into organic solvent or possibly after dilution with suitable organic solvent. This quinine-based molecular species undergoes fluorescence and there is, in theory, no requirement to separate as this fluorescence provides some level of selectivity. However, both tonic water and bitter lemon are not simple carbonated solutions of this compound. They are in fact mixtures of other organic and organo-ionic components. These include sugars, synthetic sweeteners, sorbate preservative, citric acid etc. The possible interferent effects from these upon the UV-vis absorbance-emission-coupled fluorescence system should be noted. Some methods

extract the analyte or concomitants in order to offer some level of separation. Hence, it may be possible to measure by HPLC-UV-vis spec. as HPLC provides separation and therefore some level of selectivity from other organic species present prior to selecting the UV absorbing wavelengths for quinine etc. of 250 and 350 nm.

3 Perform a t-test

$$t = \frac{\bar{x} - \mu}{s/\sqrt{n}} = \frac{2.2 - 2.06}{0.24/\sqrt{5}} = 1.304$$

t_{calc} = 1.304
t_{crit} = 2.776 (two sided for 95% confidence and n-1 degrees of freedom)
$t_{calc} < t_{crit}$ so you can retain the null hypothesis and conclude that there is no significant difference at the 95% confidence level.

4. Method of standard additions

Concentration in unknown, $x = -\frac{a}{b}$

Concentration in blank $= -\frac{a}{b} = -\frac{(-0.0501)}{0.0184} = 2.72\ \mu g\ cm^{-3}$

Concentration in sample $= -\frac{a}{b} = -\frac{(-0.3218)}{0.0186} = 17.3\ \mu g\ cm^{-3}$

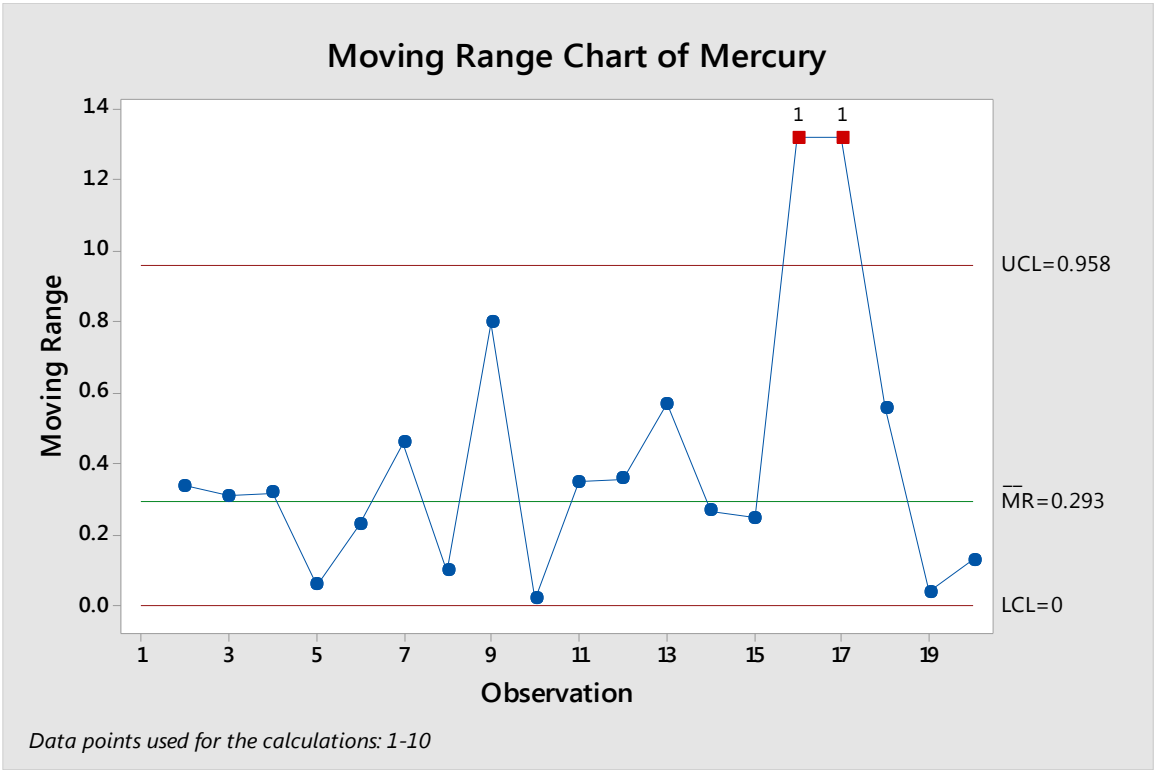
Blank corrected concentration = 17.3 – 2.72 = 14.58 $\mu g\ cm^{-3}$

5. Calculate average moving range using the first 10 QC samples, i.e. there will be 9 values

For the first 10 samples: $\overline{MR} = 0.293$
(note: there are only 9 MR values to average for the first 10 samples)

Plot the individual MR values then draw the control limits as follows:

Upper control limit	=	$3.267\overline{MR}$	red horizontal line
Target value	=	$\overline{MR}$	green horizontal line
Lower control limit	=	0	red horizontal line



A problem is normally indicated when:

1. one point falls outside the action limits **– this occurs on days 16 and 17**
2. eight successive points fall on the same side of the mean
3. six points in a row trending up or down
4. fourteen points in a row alternating up and down