ISSN 1757- 5958

amc technical briefs

Editor: Michael Thompson Analytical Methods Committee AMCTB No 40 June 2009

The Duplicate Method for the estimation of measurement uncertainty arising from sampling

In recent years there has been a renewed emphasis on the idea that sampling is part of the measurement process rather than a separate activity of little relevance to analysts. It is now recognised that the uncertainty statement for a measurement process should include contributions from both the sampling and analytical processes. A simple and cost-effective method of estimating the uncertainty that sampling contributes to the measurement process is the Duplicate Method.

The Duplicate Method is summarised here; a full explanation with worked examples is given in a recent Eurachem/CITAC Guide (Ramsey and Ellison, 2007). The method uses replicate sampling and analysis to estimate the separate contributions to the measurement uncertainty from the sampling and analytical processes. It generates estimates of the sampling variability (usually the main contribution to the sampling uncertainty) and the analytical repeatability, which are the random components of the measurement uncertainty. For the systematic components of the uncertainty, the analytical contribution can be estimated by accepted methods but the sampling bias is perforce usually ignored. The overall measurement uncertainty can then be estimated by combining the uncertainty from sampling with that from the chemical analysis. The analytical uncertainty can be estimated independently, or the value from the duplicate method used, especially if it is larger and therefore potentially more reliable.

How to implement the Duplicate Method

The Duplicate Method is usually applied by using a balanced design (Figure. 1). Random duplicate primary samples are taken at 10% ($n \geq 8$) of sampling targets. The minimum of eight duplicate samples is to ensure that the resultant uncertainty estimates are reasonably precise: a larger number would be preferable. Both duplicate primary samples undergo physical sample preparation (of the whole primary sample) and two test portions are taken from each. The test portions (4 for each sampling target) are then analysed using an appropriate analytical method under repeatability conditions.

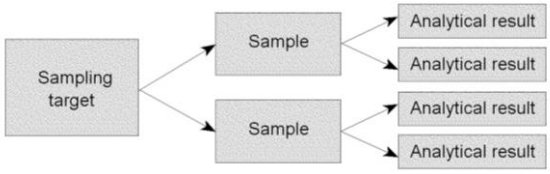


Figure 1. Design for the Duplicate Method for estimating between-sample standard deviation. Duplicate primary samples are taken from at least eight targets, and each sample is analysed in duplicate.

How duplicate samples are taken

The Duplicate Method can be applied to whatever sampling protocol is in use. Most sampling protocols include some scope for variation and the duplicates in the Duplicate Method should represent these permitted variations effectively (e.g. for soils or some foods if sampling locations are specified to within a metre, duplicates can be chosen from a different point within a metre of the first.). Where a grid or 'W pattern' is to be laid out to obtain a primary sample the starting point and initial direction are rarely specified; an effective duplicate involves an alternative starting location and initial direction (Box 1). For sampling other media, such as water or gas, the main source of heterogeneity and consequent uncertainty will usually be in the temporal domain. The duplicate sample can therefore be taken after a suitable interval, but at the same location, so as to also reflect the effect of ambiguity in the sampling protocol. Examples of how duplicates might be taken are presented in Box 1. Further ideas for including the random effects generated by the interpretation of the sampling protocol can be found in Ramsey and Thompson (2006).

(While this balanced design is normally carried out by a single sampler using a single protocol, in the Duplicate Method it can also be used by multiple samplers in a collaborative trial in sampling to estimate the between-operator contribution to the uncertainty.)

Two approaches, excluded from the basic Duplicate Method, can be used to include contributions to the uncertainty from the sampling and analytical bias. The sampling bias is either assumed to be negligible or can be estimated separately using multiple samplers/ protocols or inter-organisational trials. The analytical bias can be estimated separately by including several matched certified reference materials in the analytical batch.

Measurement interpretation

If the full balanced design has been implemented a data set similar to that presented in Table 1 will be obtained. Random components of the measurement uncertainty can now be estimated by using analysis of variance (ANOVA), and also the contributions from the sampling and analysis.

Site ID code	S1A1	S1A2	S2A1	S2A2
A	59.92	36.42	43.09	55.03
B	176.03	105.85	142.96	111.85
C	209.19	247.02	138.95	125.95
D	512.78	480.72	598.21	601.66
E	237.62	216.57	181.7	122.51
F	376.85	381.75	576.24	514.49
G	69.6	63.04	113.06	96.61
H	429.03	509.75	700.09	629.15

Table 1. Example of measurements produced from the implementation of the duplicate method. The column heading S1A1 indicates the first analytical result from the first sample: the others follow the same pattern. N.B. results shown are neither rounded (e.g., 2.68759 not 3.0) nor truncated (e.g. 0.02542 not < 0.1).

When the results include up to 10% of outliers, but are otherwise normally distributed, it may be better to use robust ANOVA. This accommodates outlying values and heavy tails by down-weighting them. Robust ANOVA can be applied by using ROBAN version 1.01 which is available from the AMC website. The output from ROBAN applied to the example data is presented in Table 2.

Mean = 276.9903				
s_{Total} = 249.7659				
	Between-target	Sampling	Analytical	Measurement
s	234.4541	79.54684	32.96293	86.106064
U%	-	57.43655	23.80078	62.17262

Table 2. Statistics derived from Table 1 by using hierarchical robust analysis of variance in the program Roban v 1.01.

Further reading

- *Measurement uncertainty arising from sampling—a guide to methods and approaches* (2007) 102pp. (http://www.eurachem.org/guides/UfS_2007.pdf)
- M H Ramsey and M Thompson, *Accred Qual Assur*, 2007, **12**, 503-507.

This Technical Brief, drafted by Dr Katy Boon, was prepared for the Analytical Methods Committee by the Sampling Uncertainty and Quality Subcommittee.

CPD Certification I certify that I have studied this document as a contribution to Continuing Professional Development.

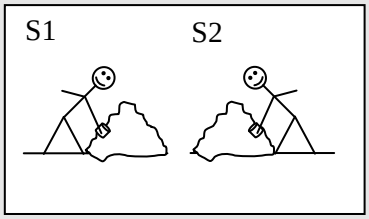
Name…….....
Signature…….……Date…….

Name of supervisor……..
Signature…….……Date……

Box 1. Examples of how to apply the Duplicate Method

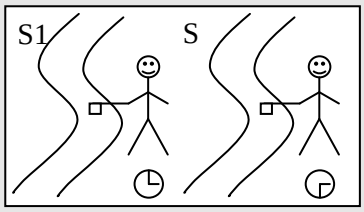
Soil

Sampling target – the volume of soil a specific depth interval of a trial pit is meant to represent, e.g. a 30 m × 30 m area between a depth of 0.5 m and 1.0 m.
Sampling protocol – the excavated material for the depth interval is placed in a heap at the side of the pit; 4 increments are taken randomly around the heap to form the primary sample.
Duplicate sample – 4 more increments are taken from a new set of randomly selected points around the heap.



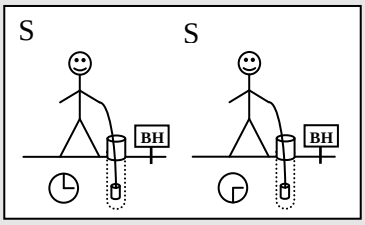
Water

Sampling target – The water flowing past a sampling point.
Sampling protocol – Collect a primary sample from the sampling point once during a specified hour.
Duplicate sample – Collect a second primary sample another time within that hour.



Landfill gas

Sampling target – The gas produced from the area a borehole is intended to represent.
Sampling protocol – Measure the concentration of the analyte of interest using a portable gas analyser once on a particular day.
Duplicate sample – Take a second reading at the same borehole at another time during that day.



Food

Sampling target – 1 bay of Iceberg lettuce grown under glass.
Sampling protocol – one composite sample formed of 10 heads of lettuce from each bay, taken from points along a W shape.
Duplicate sample – a second 10-head composite samples is taken from a W shape with a different starting point and orientation to the original.