

## A simple fitness-for-purpose control chart based on duplicate results obtained from routine test materials

There is a simple graphical method for assessing and controlling repeatability precision from a moderate number of duplicated analytical results. The data are obtained from test materials (as opposed to control materials), and the chart differs from the classical control chart because it depends on an independent fitness-for-purpose criterion. This 'Thompson-Howarth duplicate chart'<sup>1</sup> has been in use for many years in the geo-analytical community, but is quite general in its applicability. The method allows for the fact that analytical precision varies with the concentration of the analyte. It has been found to be especially helpful in situations where statistical control cannot be assumed, for example, in 'ad-hoc' analysis or when a well-established method is used infrequently.

### Statistical control and fitness for purpose

The classical Shewhart control chart, as used by analysts for internal quality control (IQC),<sup>2</sup> is based on the idea of statistical control, that is, that errors in successive runs of an analytical system can be described adequately by a given normal distribution. Often, however, we cannot use the idea of statistical control, because the analysis being undertaken is unique or attempted only infrequently. In such instances, however, we still need some kind of IQC, to ensure that the uncertainty of the measurement falls within bounds defined by fitness for purpose (FFP).

Regardless of whether or not statistical control is applicable, it is possible to compare the closeness of duplicated analyses with a specification prescribed by a predetermined FFP criterion. If we wish to assess repeatability precision, we can simply conduct duplicate analyses on some or all of the test materials within a run. The results obtained by analysing many different, but typical, materials in duplicate in a random sequence are indeed more representative of the precision characteristics of the analytical system than results from one or two control materials with a greater number of replications. Many analysts conduct duplicate analyses as a matter of routine, and in such circumstances, no extra effort is required.

### Rationale of the T-H chart

Supposing that fitness for purpose requires the analytical system to provide results with a repeatability standard

deviation of  $s_r$ . The difference  $d = x_1 - x_2$  between two duplicated measurements ( $x_1, x_2$ ) should have a standard deviation of  $s_d = \sqrt{2}s_r$ . Under the assumption of the normal distribution, we can define various bounds for  $|d|$ , the absolute difference between  $x_1$  and  $x_2$ . For example, we would expect on average half of the absolute differences to fall above the 50<sup>th</sup> percentile, given by

$$P_{50} = 0.6745 \times \sqrt{2}s_r = 0.954s_r$$

and 5% of them to fall above

$$P_{95} = 1.960 \times \sqrt{2}s_r = 2.772s_r$$

The multipliers of  $s_r$ , used for calculating the bounds, are derived from the normal distribution: a useful selection is given below.

Percentile	Factor
50th	0.954
90th	2.326
95th	2.772
99th	3.643
99.9th	4.654

If the performance of the analytical system is not as good as that required by the FFP criterion then, in the long term, there will be higher proportions of the data than expected falling above the previously defined limits. So the T-H monitoring system rests on: (a) defining limits for  $|d|$  based on the FFP criterion; and (b) deciding whether the duplicated data conform to it, by seeing how the differences lie in relation to the specified percentile limits.

However, there is a complication. In most analytical systems the repeatability standard deviation increases as a function of the concentration of the analyte. Therefore, if we are analysing unknown test materials containing variable concentrations of analyte, the analytical precision, characterised by  $s_r$ , will not remain constant. Consequently, we cannot have a single specification for percentiles of  $|d|$ . Fortunately the variation in precision can usually be modelled adequately by relating  $s_r$  to the analyte concentration  $c$  as follows<sup>3</sup>:

$$s_r = c_L/3 + Bc,$$

where  $c_L$  is the repeatability detection limit and  $B$ , the 'asymptotic RSD', is the relative standard deviation to which the results tend at high ( $c \gg c_L$ ) concentrations of analyte. (The form of the model equation as given is not correct from a theoretical standpoint,<sup>3</sup> but it performs perfectly well in practice because the mismatch is small.) The FFP criterion can be specified in a similar way, by setting percentile bounds on  $|d|$  as a function of  $c$ . For example, the 50th percentile of  $|d|$  would be given by

$$P_{50} = 0.954(c_L/3 + Bc),$$

where, in this case,  $c_L$  and  $B$  are pre-defined by end-user requirements.

These control limits are realised by plotting the functions as lines on a graph. We place experimental points on such a graph by plotting the absolute difference between duplicated values against their mean value. If the concentration range spans orders of magnitude, log/log axes are best used since, if the measured concentrations are well above the detection limit of the method, the control bounds are straight lines, as in Example 1.

#### Example 1

In this instance, the specified FFP criterion is  $B = 0.05$ , *i.e.*, we require an RSD of 5% irrespective of the concentration. The 50th percentile more or less bisects the group of datapoints (Fig. 1), and none of the points fall above the 95th percentile. These data are therefore consistent with a system performing broadly in line with the FFP criterion.

#### Example 2

In the second example, the FFP criterion is defined by a detection limit of 15 units and an asymptotic RSD of 5%, which gives rise to curved percentiles on the log-log plot (Fig. 2). In this particular example, the results fall into two groups over the concentration range. Because a majority (9/11) of the points in the lower concentration group fall above the 50th percentile, and 3/11 of them fall above the 95th percentile, the analytical system must be performing less well than the FFP requirement over that concentration range. That is an indication that the detection limit achieved by the analytical method being used is not as low as the FFP specification. The points of the higher group are more or less bisected by the 50th percentile and hence the analytical system conforms with the criterion over that part of the concentration range.

Figure 1

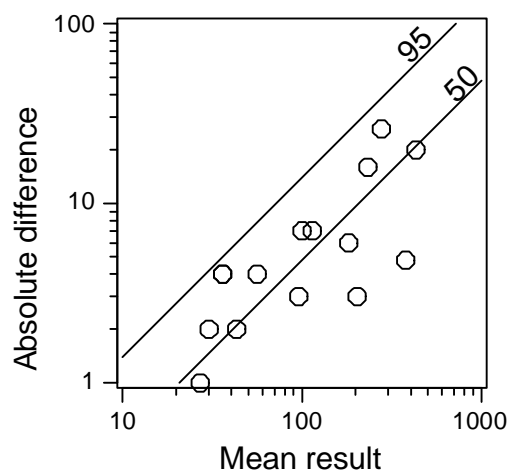
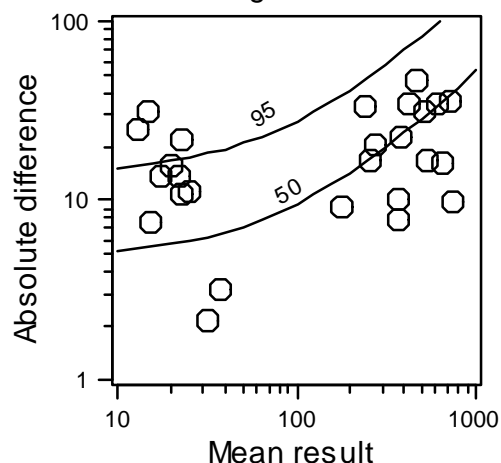


Figure 2



#### References

1. M Thompson and R J Howarth, *J. Geochem. Explor.*, 1978, **9**, 23-30.
2. R J Howarth, *Analyst*, 1995, **120**, 1851-1873.
3. M Thompson, *Analyst*, 1988, **113**, 1579-1587.

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