ISSN 1757- 5958

amc technical briefs

Editor: Michael Thompson Analytical Methods Committee AMCTB No 49 March 2011

Sporadic blunders

Sporadic blunders, affecting only one or a few test materials in a run of analysis, will seldom be detected by routine internal quality control (IQC). This is an important problem because blunders may not be particularly rare. IQC works by the analysis in each run of one or more control materials that are closely similar in composition to the routine test materials. The control materials are treated in exactly the same way as the test materials and act as a surrogate for them. Any noteworthy problem with quality will be manifest in the IQC results as a lapse in statistical control. However, at its best, IQC will detect only problems that systematically affect the whole run.

The problem

Sporadically-occurring large errors in analytical results may be more common than generally thought. It is impossible to get statistics because blunders go undetected—if they are detected they are replaced with valid results. However, in a recent study of proficiency test results from year 2006, encompassing 50 different matrices/analyte combinations and a large population of laboratories in the food sector, the proportion of outliers found was 4.7 % (117 out of 2507 results) [*]. An example is shown in Figure 1. Some laboratories will consistently do better than others and therefore produce a smaller proportion, but all participants knew that they were under test and were presumably keen to get a good z-score. Moreover, most of the laboratories (65%) claimed to be using an accredited method. Even though the statistic is not a direct indicator of the average proportion of sporadic blunders in a particular laboratory, 4.7% is an alarming level.

Sporadic blunders probably comprise the most pervasive and most serious type of problem encountered in analytical results. They contribute to the false impression that analytical results are too often unfit for purpose by virtue of overlarge uncertainty. In reality, most analytical systems are already fit for purpose in that, if we apply the procedure correctly to the specified type of test material, we get a result that has a near optimal uncertainty for the end-user. It is sporadic blunders that make an otherwise fit-for-purpose method seem to be unreliable.

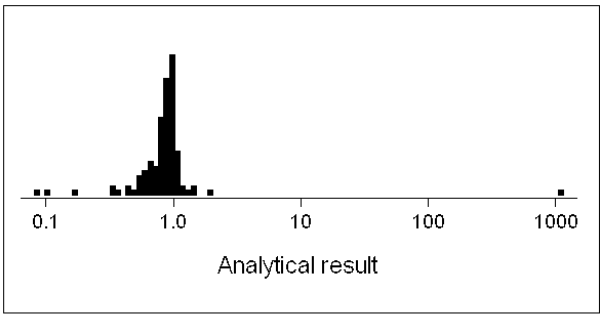

Figure 1. Results (cadmium in a foodstuff, mg/kg) from 116 laboratories in a round of a proficiency test.

The causes of sporadic blunders

Sporadic blunders can be caused by both chemical and clerical mistakes. A list of the most likely causes includes the following. (Remember that we are not considering systematic actions affecting a whole run, only actions affecting individual test portions.)

- Addition of a reagent or diluent is omitted, or the reagent added twice, or in the wrong amount.
- A stage of the procedure is omitted or misapplied in some way.
- A test material of a type that is outside the scope of the validation of the method is included in the run.
- The test portion or the test solution is contaminated (for instance, by use of an insufficiently cleaned container).
- Some of the test portion or test solution is lost by careless handling.
- There is a transient instrumental problem (such as a blocked nebuliser that clears itself, or a memory effect).
- A result is recorded incorrectly.
- Two or more test portions are mislabelled or switched in the analytical sequence.

[*] *Accred Qual Assur*, 2009, **14**, 73-78. Outliers are defined in this paper as results deviating from the robust mean by more than 3.5 times the robust standard deviation. In a normal distribution, these limits would exclude about 0.05 % of results.

How sporadic blunders can be detected and eradicated

Many of these events can be attributed to a lapse of concentration in the complex and exacting series of operations in a typical analysis. They can be minimised by proper attention to training and supervision, features involved in accreditation. Pertinently, in the study referred to previously, the incidence of outliers from laboratories accredited for the method was about half of that encountered where no accreditation was claimed.

But we all suffer occasional lapses of attention. Moreover, even fully automated systems can go wrong, as many analysts have found to their dismay. So it would be useful to have methods available by which sporadic blunders could be detected at an early stage, especially results on which critical decisions rest. Several such measures are suggested here. They are not all generally applicable or equally effective, and they all involve more work for the analyst.

Duplication. *Analyse all of the test materials in duplicate in a run, in a completely random order, and test for abnormal deviation between corresponding results.*

The probability of both results of a duplicate pair being sporadic blunders of the same type is small in all but the smallest runs. If the repeatability standard deviation σ_r is reasonably well-estimated (as it would be in a validated method), we could regard as suspect any duplicate results where the absolute difference between them exceeded about $2.8\sigma_r$. Differences greater than $4.2\sigma_r$ require attention. (These values roughly correspond in probability to warning and action limits in Shewhart charts. Some attention must be paid to the concentration of the analyte, as σ_r will vary with concentration.) If σ_r is poorly estimated, simply look for outlying differences. The questioned test material should be reanalysed in the next run, and the new result should enable the analyst to identify the correct result[*].

Running samples in a completely random order is perfectly feasible and trouble-free. Apart from giving realism to the value of σ_r , it reduces the chance of sporadic problems affecting duplicates. If the duplicates were adjacent in the sequence, there would be a greater chance of a sporadic blunder affecting both. This method will not detect problems relating to a test material outside the defined scope of the validation[†].

[*] Guidance on handling discrepant results can be found in ISO 5725. However, the comparison of results replicated run-to-run cannot be based on σ_r alone. A run-to-run variance component is also involved, and this is not covered in the Standard.)

[†] Averaging results replicated under repeatability conditions is unlikely to reduce the uncertainty to a consequential degree.

Reference analyte. *Add a fixed amount of a reference analyte to each test portion.*

The concentration of the reference analyte native in the test materials should be negligible. Determine the reference analyte alongside the real analyte. An anomalous result for a reference analyte points to a sporadic event. The reference analyte could be an internal standard where one is part of the original method. This method may be useful for detection of unexpected matrix effects in a test material outside the scope of the system definition, but would fail to detect other problems such as mislabelling.

Anomalous result. *Review the results in the light of past experience.*

Set aside for reanalysis any sample that gives a result outside the previously established 95% confidence interval for that type of material. Then review the results in relation to critical decision limits that apply in the application sector. Repeat the analysis if a result is close to such a limit.

Further reading

AMC Technical Briefs 46 (2010). Internal quality control in routine analysis.

This Technical Brief was prepared for the Analytical Methods Committee by the Statistical Subcommittee (Chair Prof J N Miller)

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……

Other AMC products can be found on www.rsc.org/amc/

You can help the AMC in the production of AMC Technical Briefs by posting comments, queries and suggestions for new topics on "MyRSC". You can find this via www.rsc.org/myrsc. *After you have logged in, go to the "Group" called "Analytical Methods Committee—Announcements and Discussions".*