amc technical briefs

recommendation

The estimation and use of recovery factors

The use of recovery information to correct analytical results has been a contentious issue in the past. Some analysts have regarded correction for recovery as a natural extension to the analytical method, while other have spurned the practice as akin to adjusting the results in an illegitimate manner. Moreover practice varies within different sectors of analysis. However, recent developments in the international forum have shown how to resolve these difficulties. The key to this resolution lies in the distinction between 'rational' and 'empirical' methods, discussed overleaf. The whole topic is documented in 'Harmonised Guidelines for the Use of Recovery Information in Analytical Measurement' (Pure Appl. Chem., 1999, 71, 337-348), sponsored by IUPAC, ISO and AOAC International.

Recommendation

- Quantitative analytical results should be corrected for recovery unless there are specific reasons for not doing so (for example, the method is acknowledged to be 'empirical', the method is defined in law, or the recovery is known to be 100 %).
- When a recovery correction is to be applied, the method of estimating the recovery should be specified in the method protocol.
- Recovery factors (for 'rational' methods) should be estimated as part of method validation, whether or not they are to be used for correction.
- Internal quality control charts for recovery should be established for routine analysis.

Rationale

The estimation of the recovery of an analyte is a well established and essential part of validating an analytical method. Recovery information is especially important in ultra-trace analysis, including such difficult fields as the determination of pesticide residues and veterinary drug residues.

It is well recognised that methods available for estimating recovery may be unsatisfactory in some circumstances. One commonly used method of estimation is to apply the analytical method to two identical portions of the test material, one of which is spiked with a known mass of the analyte, m_{spike}.

The recovery estimate (the 'surrogate recovery' or 'marginal recovery') is given by:

$$R = \left(m_{total} - m_{native}\right)\big/m_{spike},$$

where m_{total} and m_{native} are the masses of analyte found in the spiked and unspiked portions respectively. The problem is that the surrogate recovery may not match that of the native (or 'incurred') analyte. For example the native analyte might be chemically bonded to the substrate while the spike is present as the free analyte. The two forms may not partition equally in a separation procedure.

Regardless of the problems of its estimation, a recovery estimate is a useful piece of information and is often part of the analytical result reported to the end-user. There is no doubt surrounding the value of this practice. However, there has been controversy about whether it is a valid practice to take the matter a stage further. If we extract a concentration c of analyte from the test material, and we estimate the recovery of the analyte to be R, is it not true that the best estimate of the concentration of the analyte is simply c/R? Let's see what analysts have to say about this.

Arguments used for correction

- The purpose of chemical analysis is to obtain an estimate of the true concentration of the analyte in the test material. The true concentration can only be estimated when significantly low recoveries have been corrected.
- An uncorrected bias due to low recovery means that results will not be universally comparable, not transferable, and therefore unfit to support mutual recognition.

• Correcting for recovery is mathematically isomorphic with generally accepted techniques such as internal standardisation and isotope dilution, and is therefore not suspect in principle.

• Although some uncertainty is always associated with the process of estimating recovery correction factors, such uncertainty can be estimated and incorporated into the combined uncertainty of the corrected result.

Arguments used against correction

• Estimated recoveries based on spiking and allied methods may be higher than the true recovery of the native analyte. Corrected analyte concentrations would therefore tend to have a negative bias.

• Estimated recovery factors are suspect because recovery may differ among matrices and also vary with the concentration of the analyte.

• Small deviations from unity in recovery estimates could result from random errors rather than systematic loss of analyte. (This accounts for recovery estimates greater than unity that are often encountered.) In this situation, applying a correction would incorrectly inflate the absolute uncertainty of the corrected result.

• Estimates of recovery often have a high relative uncertainty. This sometimes causes a recovery-corrected result to appear (falsely) to have a much higher relative uncertainty than the uncorrected result. This high relative uncertainty may in turn undermine the credibility of analytical science.

• Some legislation imposing maximum limits on contaminants is framed on the understanding that uncorrected results will be used for enforcement.

Rational and empirical methods

Most of the arguments listed above command at least some consideration, so we can deduce that the decision (whether or not to correct for recovery) must depend on the circumstances. The technically important circumstance is whether the analytical method is regarded as *rational* or *empirical.*

In a 'rational method' the analyte is a discrete well-defined chemical entity, copper for example. There are many different physical principles that can be utilised for the determination of copper in (say) soil, but so long as we avoid loss of analyte, contamination, and matrix effects, all of these methods will tend to give the true concentration of copper. This value is found by comparing the extent of the physical property in question with that obtained with dilutions of pure copper, through the process of calibration. The result is therefore traceable *inter alia* to the pure analyte. If we want our result to be rational, then we must clearly correct for recovery. All rational methods are potentially equivalent.

> ## "All rational methods are potentially equivalent"

In an 'empirical method' the analyte is not so well defined. An example would be the determination of EDTA-extractable copper in soil. EDTA is regarded as capable of extracting organically bound metals from soil, so the proportion extracted of the total copper present (the recovery, in fact) would depend on the nature and proportion of organic matter in the particular sample of soil. Here the result is dependent on the exact method employed—different methods give different results. Therefore, results obtained without correction for recovery are necessarily empirical.

> ## "Results obtained without correction for recovery are necessarily empirical"

Finally…

The good news is that, as a corollary of the above, if we are prepared to accept that we are using an empirical method, we do not need to correct for recovery. The bad news is that different empirical methods are unlikely to be comparable. Moreover, if we want comparability among users of a single empirical method, the procedure has to be defined in great detail. Furthermore, using an empirical method goes against the modern trend for specifying method performance in regulatory documents, rather than specifying particular methods.

This Recommendation was prepared for the Analytical Methods Committee by the Statistical Subcommittee (Chairman M Thompson).

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