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USE OF THE TERMS "RECOVERY" AND "APPARENT RECOVERY" IN ANALYTICAL PROCEDURES

(IUPAC Recommendations 2002)

Prepared for publication by
DUNCAN THORBURN BURNS[1,‡], KLAUS DANZER[2], AND ALAN TOWNSHEND[3]

[1]Department of Analytical Chemistry, The Queen's University of Belfast, Belfast, BT9 5AG, N. Ireland, UK; [2]Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University of Jena, Lessingstrasse 8, D-07743 Jena, Germany; [3]Department of Chemistry, The University of Hull, Hull, HU6 7RX, UK

‡Corresponding author

Use of the terms "recovery" and "apparent recovery" in analytical procedures

(IUPAC Recommendations 2002)

Abstract: The terms **recovery** and **apparent recovery** are recommended to avoid confusion caused by the use of the term **recovery** to cover two distinct situations. These situations deal with: (a) the **yield** of a preconcentration or extraction stage of an analytical process (where **recovery** is recommended) and (b) the quantity **observed value/reference value**, obtained using an analytical procedure that involves a calibration graph (where **apparent recovery** is recommended).

DISCUSSION

At present, the term **recovery** is used in two distinct contexts:

I. The terms **recovery** [1–4] or **recovery factor** [4,5] (symbol R) are at present used to indicate the yield of an analyte in a preconcentration or extraction stage in an analytical method:

$$R_A = \frac{Q_A(\text{yield})}{Q_A(\text{orig})} \tag{1}$$

where Q_A(orig) is the known original and Q_A(yield) the recovered quantity of the analyte A.

If R_A is measured using a standard addition or spike procedure,

$$R_A = \frac{Q_A(O+S) - Q_A(O)}{Q_A(S)} \tag{2}$$

where Q_A(S) is the quantity of analyte A added (spike value) and Q_A(O + S) the quantity of A recovered from the spiked sample and Q_A(O) from the original sample. In all uses of spiked or standard addition procedures, it is essential to ensure that uniform chemical and/or isotopic distribution is achieved between the material added and that originally present in the sample. The concentration of analyte in the spike should be sufficiently high so as to minimize disturbance, by dilution, of the matrix. It should be noted that the addition of a spike only checks that part of a procedure after the addition of the spike.

II. **Recovery** is also used to denote the ratio of observed value, x(obs), obtained from an analytical process via a calibration graph, divided by the reference value, x(ref) [1,6,7]. The reference value may be that of a certified reference material or the increased amount of analyte observed from the addition of a known amount of analyte to the test sample [8,9]:

$$R'_A = \frac{x(\text{obs})}{x(\text{ref})} \tag{3}$$

or

$$R'_A = \frac{x(\text{obs}, O+S) - x(\text{obs}, O)}{x(S)} \tag{4}$$

where x(obs, O + S) is the observed value for the spiked sample, x(obs, O) the observed value for the original, unspiked sample, and x(S) the value for spike.

In some cases, it is not clear from the text which sense of the term is implied [10,11].

The second use of the term **recovery**, observed value/reference value, should be distinguished from the first use, i.e., for the yield of an analyte as defined in eqs. 1 or 2. This is because for an analytical process with a linear or linearizable [12] calibration graph, 100 % recovery does not require 100 % yield for any separation or preconcentration stage. The requirement is that the yield for the test and the calibration be the same. For example, in the spectrophotometric determination of the amount of analyte A after solvent extraction of the analyte A whose yield R_A, and/or molar decadic absorption coefficient, ε, depend on the solvent, absorbance values, A, of calibration samples and test samples vary by the same factor, $R \cdot \varepsilon$, for constant path lengths, l. Thus, the interpolated concentration value for the test sample is independent of the calibration graph slope (see Fig. 1, where subscripts 1 and 2 refer to solvents 1 and 2, respectively).

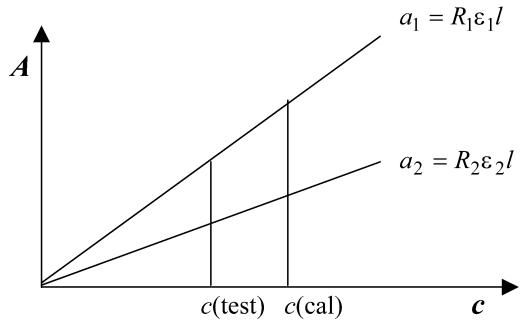

Fig. 1 For a linear calibration graph, c(test) is independent of slope a.

The argument is similar for the method of standard addition, which gives compensation for matrix effects on yield. For determination by atomic absorption spectrophotometry, R is directly dependent on sample loss on nebulization and fraction of analyte present as atoms.

Hence, it is recommended that the term **recovery** be used for yield, see eq. 1,

$$R_A = \frac{m_A(\text{yield})}{m_A(\text{orig})} = \frac{m_A(\text{recov})}{m_A(\text{orig})} \tag{5}$$

where m_A(yield) and m_A(recov), respectively, are the masses of analyte A recovered and m_A(orig) the original mass of analyte in sample. It is also recommended that **apparent recovery** be used for information obtained via a calibration graph

$$R'_A = \frac{x_A(\text{exp})}{x_A(\text{theor})} \tag{6}$$

where x_A(exp) is the value experimentally obtained from calibration graph and x_A(theor) is a reference, known or theoretical value.

It should be noted that an apparent recovery, $R' = 100$ %, obtained using a single reference material or single spike addition experiment does not indicate the absence of systematic error or that a procedure has successfully been validated [3,13].

In the presence of an additive and a proportional systematic error (bias), agreement between a measured value, c(meas), and the true or certified reference value, c(ref) may appear fortuitously. This is illustrated by the validation function (recovery function) shown in Fig. 2.

The validation functions are determined by normal linear regression. At the point of intersection (2) c(meas) = c(ref) and therefore $R' = 100$ %, whereas at point (1) c(meas) > c(ref), $R' > 100$ %, and at point (3) c(meas) < c(ref), $R' < 100$ %.

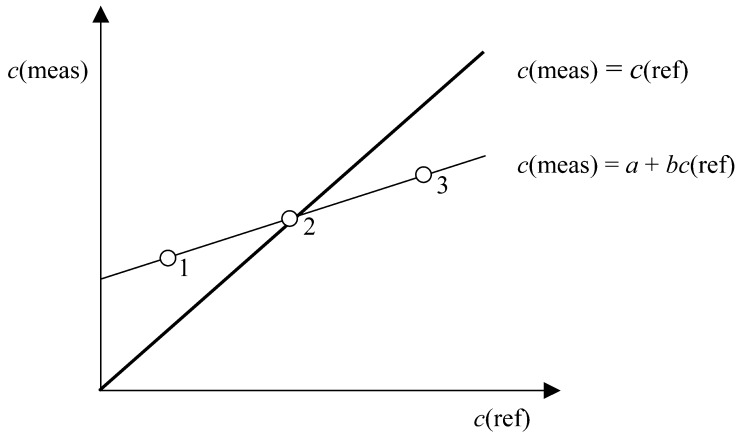

Fig. 2 Ideal validation function c(meas) = c(ref): no systematic error, and real validation function c(meas) = a + bc(ref): presence of an additional error a and a proportional error b.

Thus, methods should be validated by the use of more than one reference material, or by standard addition, to cover a suitable range of values of amounts of analyte.

RECOMMENDATIONS

The definitions stated below are recommended:

RECOVERY or **RECOVERY FACTOR:** yield of a preconcentration or extraction stage of an analytical process for an analyte divided by amount of analyte in the original sample.

Note: If Q_A(yield), Q_A(orig) are the recovered and original quantities of analyte A, then the recovery is $R_A = Q_A(\text{yield})/Q_A(\text{orig})$. Alternatively, if Q_A(S), Q_A(O), Q_A(O + S) are, respectively, the quantity of A added (spike value), the quantity of A in the original sample, and the quantity of A recovered from the spiked sample, then $R_A = [Q_A(\text{O + S}) - Q_A(\text{O})]/Q_A(\text{S})$.

APPARENT RECOVERY: observed value, x(obs), derived from an analytical procedure by means of a calibration graph divided by reference value, x(ref).

Note: If x_A(S), x_A(O), x_A(O + S) are, respectively, the quantity of analyte A added (spiked value), the quantity of A in the original sample and the quantity of A recovered from the spiked sample, then the apparent recovery becomes $R_A = [x_A(\text{O + S}) - x_A(\text{O})]/x_A(\text{S})$.

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