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COMMISSION ON GENERAL ASPECTS OF ANALYTICAL CHEMISTRY<sup>‡</sup>

**RECOMMENDATIONS FOR THE USE OF THE TERM  
“RECOVERY” IN ANALYTICAL PROCEDURES**

(IUPAC Recommendations 2001)

*Prepared for publication by*

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# RECOMMENDATIONS FOR THE USE OF THE TERM “RECOVERY” IN ANALYTICAL PROCEDURES

(Technical Report)

*Prepared for publication by*

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## Summary

The terms **recovery** and **apparent recovery** are recommended to avoid confusion caused by the use of the term **recovery** to cover two distinct situations. Namely, to deal with the **yield** of a preconcentration or extraction stage of an analytical process and the **ratio, observed value/reference value**, obtained using an analytical process with calibration graph.

## Discussion and recommendations

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

I. The terms **recovery** [1a,2-4] or **recovery factor** [4,5] are at present used to indicate the yield of an analyte in a preconcentration or extraction stage in an analytical method:

$$R_A = \frac{Q_{A_{yield}}}{Q_{A_{orig}}} \quad (1)$$

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,

$$R_A = \frac{Q_{A_{O+S}} - Q_{A_O}}{Q_{A_S}} \quad (2)$$

where  $Q_{A_S}$  is the quantity of analyte  $A$  added (spike value) and  $Q_{A_{O+S}}$  the quantity of  $A$  recovered from spike sample and  $Q_{A_O}$  from the original sample. In all uses of spiked or standard addition procedures it is essential to ensure that 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 minimise disturbance, by dilution, of the matrix. It should be noted that the addition of a spike only checks that part of a procedure post 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 compared to the reference value [1b,6,7],  $x_{ref}$ , for example, that of a reference material certified value or from the increase amount of analyte observed from the addition of a known amount of analyte to a test sample [8,9]:

$$R'_A = \frac{x_{obs}}{x_{ref}} \quad (3)$$

or

$$R'_A = \frac{x_{obs_{O+S}} - x_{obs_O}}{x_s} \quad (4)$$

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 yield. This is because for an analytical process with a linear or linearisable [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 after solvent extraction of an analyte A whose yield  $R_A$ , and/or molar decadic absorption coefficient,  $\epsilon$ , depend on the solvent the observed absorbance values of calibration samples and test sample vary by the same factor,  $R \cdot \epsilon$ , for constant path lengths,  $l$ . Thus the interpolated concentration value for the test sample is independent of calibration graph slope, see Fig. 1.

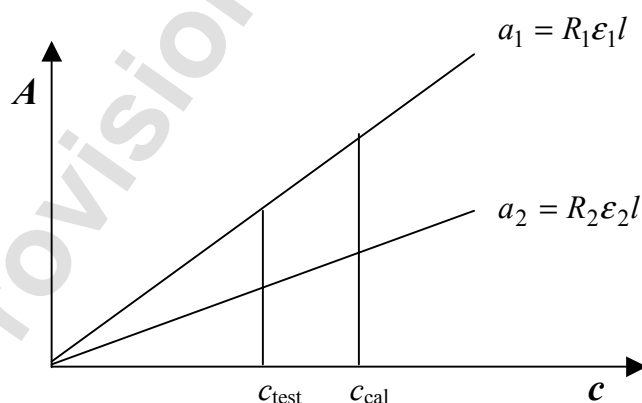


Fig. 1. For a linear calibration graph  $c_{test}$  is independent of slope  $a$

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 nebulisation and fraction of analyte present as atoms.

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

$$R_A = \frac{m_{A_{yield}}}{m_{A_{orig}}} = \frac{m_{A_{recov}}}{m_{A_{orig}}} \quad (5)$$

where  $m_{A_{yield}}$  and  $m_{A_{recov}}$ , respectively, is the mass of analyte  $A$  recovered and  $m_{A_{orig}}$  the original mass of analyte in sample, and that **apparent recovery** be used for information obtained via a calibration graph

$$R'_A = \frac{x_{A_{exp}}}{x_{A_{theor}}} \quad (6)$$

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 as shown by the validation function (recovery function) shown in Fig. 2.

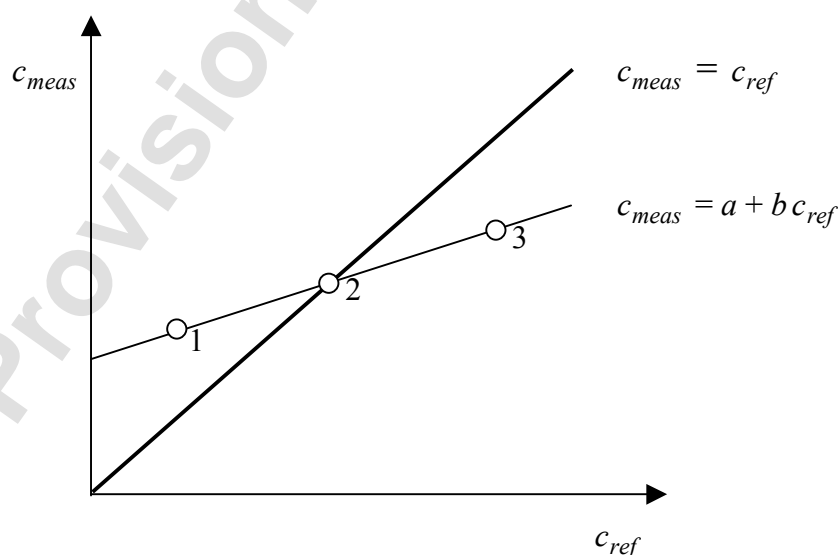


Fig. 2. Ideal validation function  $c_{meas} = c_{ref}$  : no systematic error and real validation function  $c_{meas} = a + b c_{ref}$  : presence of an additional error  $a$  and a proportional error  $b$

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)  $c_{meas} < c_{ref}$ ,  $R' < 100\%$ .

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

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