

Some remarks on the recovery method

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Abstract. The recovery method is discussed theoretically in terms of its similarity to the standard addition method. It has been revealed that analytical information typical of the latter method can be obtained using the recovery method.

Key words. recovery method – standard addition method.

One of the approaches used for evaluation of the accuracy of analytical results is the so called the recovery test [1]. The procedure commonly carried out in this case is illustrated in figure 1. A sample examined is dosed by an analyte in well defined concentration, ΔC_B , and measurements are performed for a sample before and after dosage. Both signals are related to the analytical calibration line, A, prepared beforehand (usually using a pure analyte) and the corresponding concentration difference, ΔC_A , is estimated. The recovery of the analyte, RV , is calculated from:

$$RV = \frac{\Delta C_A}{\Delta C_B} * 100\%. \quad (1)$$

The analytical method assayed is considered accurate if the recovery found is close to 100%. It is evident that such a result can be achieved only if the signal produced by the analyte added to the sample is equal to the signal produced by the same amount of the analyte in the standards. Otherwise a recovery more or less different of 100% has to be expected (see Fig. 1), particularly because of the interference effect occurring in the sample,

It is important to note that the recovery method (RM) in the form presented above bears a resemblance to the standard addition method (SAM). The fact is that the laboratory procedures of both methods are the same in principle, except that the calibration line A does not need to be prepared in the SAM (compare Figs. 1 and 2). Besides, the application of both methods is based on the same prerequisites, namely:

- the analyte should be added to the sample in such a way as to keep the concentration of the interferents and the analyte originally present in the sample constant,
- the analyte originally present in the sample and the analyte added to the sample should behave identically during measurements [2].

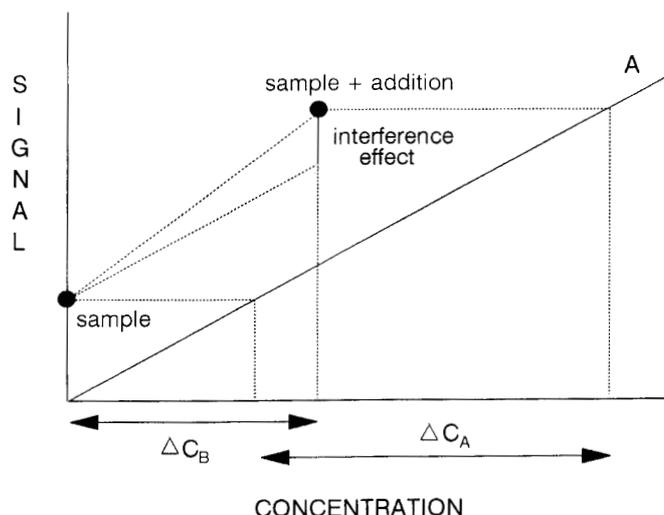


Figure 1. The principle of the recovery method; the concentration difference, ΔC_A , found from the calibration line A is not equal to the concentration added, ΔC_B , because of the interference effect.

However, the above conditions involve rather different expectations of both methods. If the RM is used the analyte added is believed to produce a signal so great as expected (assuming that the interferences are absent), but if the SAM is used the interference effect is expected to be compensated for (assuming that multiplicative and not additive interferences are present [2]). Consequently, the SAM, unlike the RM, is considered the calibration method, since the analyte is added in order to prepare the calibration line B (sloped differently than line A because of the interference effect) and to estimate the analytical result, C_B , which is believed to be close to the true analyte concentration in the sample (see Fig. 2). In other words, although both methods are performed in a similar manner, they are considered differently

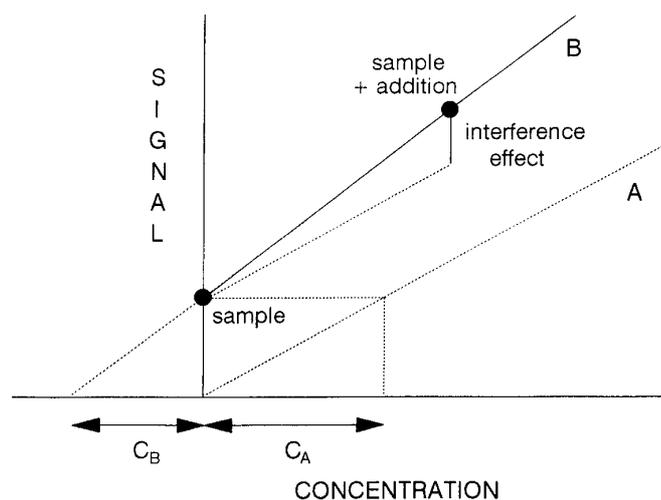


Figure 2. The principle of the standard addition method; the calibration line B takes the interference effect into account and therefore the analytical result, C_B , is believed to be more accurate than result C_A obtained from the calibration line A.

with respect to their analytical role and to interpretation of the results obtained.

What is suggested here on the basis of above deduction is to exploit the calibration potentials provided by the SAM at the same time as the accuracy is tested by the RM. To do this no experimental activities in addition to those typical for the RM are needed but, owing to the wider interpretation of the results obtained, some information additional to the recovery values can be achieved which is very important from the analytical point of view. In particular:

- if the analyte concentration in a sample, C_A , is estimated from the calibration line A (see Fig. 2), it may be easily proved that the analytical result, C_B , can be found from:

$$C_B = \frac{C_A}{RV} * 100. \quad (2)$$

- if the calibration line B is prepared, the interference effect can be evaluated by comparison of the slopes of lines A and B [3],

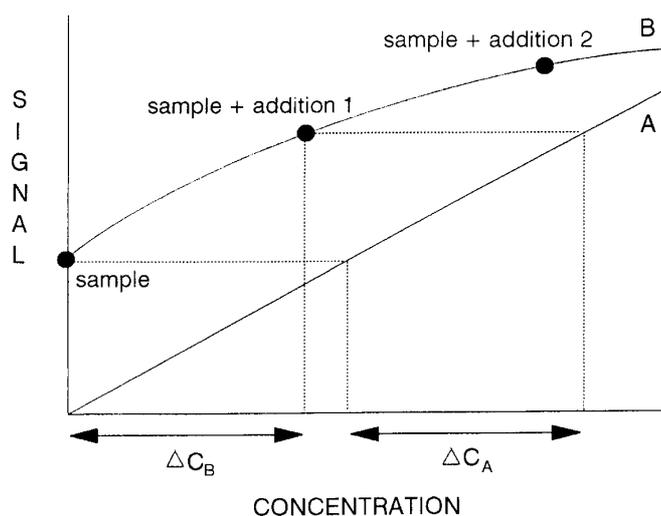


Figure 3. The recovery method with two additions of an analyte; if the calibration line B is curved, 100 % recovery can be detected with the use of the first addition ($\Delta C_A = \Delta C_B$) but different result is obtained with the use of second addition.

- if the recovery is examined using more than one addition of an analyte (which is indeed done quite often in practice), then the curvature of line B (caused e.g. by the interference effect of a complex nature) can be detected (see Fig. 3). In the latter case the risk of achieving a 100% recovery on the basis of only one particular range of analyte concentration (i.e. rather accidentally) can be also avoided (see Fig. 3). When line B is curved, the SAM can be still successfully used for calibration purposes, giving analytical results, C_B , quite reliable in terms of accuracy and precision [4].

It seems that the above remarks on the recovery method are not widely applied and this is the reason for the discussion presented.

References

1. International Union of Pure and Applied Chemistry, *Spectrochim. Acta* **1978**, 247, 33B.
2. Welz, B. *Fresenius Z. Anal. Chem.* **1986**, 325, 95.
3. Kościelniak, P.; Janiszewska, J. *Lab. Robot. Autom.* **1997**, 47, 9.
4. Kościelniak, P. *Chemom. Intell. Lab. Syst.* **1999**, 275, 47.