

German standard methods for the examination of water, waste water and sludge

**General information (group A)**

Verification of equivalence of two analytical methods by comparing the results obtained with an identical sample (known matrix) (A 71)

**DIN****38 402**

Part 71

Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung; Allgemeine Angaben (Gruppe A); Gleichwertigkeit zweier Analysenverfahren aufgrund des Vergleichs der Untersuchungsergebnisse an der gleichen Probe (gleiche Matrix) (A 71)

*In keeping with current practice in standards published by the International Organization for Standardization (ISO), a comma has been used throughout as the decimal marker.*

This standard has been prepared jointly with Study Group *Wasserchemie* (Water Chemistry) of the *Gesellschaft Deutscher Chemiker* (German Chemists' Society) (see Explanatory notes).

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**1 Field of application**

This standard describes the procedure used in water analysis to assess the equivalence of analytical results obtained by two different analytical methods for a known matrix. Analytical methods which cannot be calibrated by means of one function can only be verified as described in sub-clause 5.2.2 (e.g. when determining COD, BOD, DOC, TOC, AOX).

Two analytical methods shall be deemed to yield reproducible results, if these are obtained via automated or mechanized stages of a method for determining individual substances, when the matrix is comparable (e.g. in the case of ground or surface water). Verification of reproducibility can be simplified by evaluation in accordance with sub-clause 5.2.2, items a) and c).

Proof of equivalence as defined in this standard shall be furnished if parameters (e.g. COD, BOD) defined by convention are to be determined by methods deviating from the agreed method for each case. By deviation is meant, for example, modification of the type and quantity of the reagents used, modified reaction times and/or reaction temperatures, different procedures in sample preparation, different methods of stabilization, different enrichment and digestion methods, and different automated or mechanized stages, or a change in the detection technique which departs from the agreed methods.

**2 Scope**

An analytical result can be distorted by accidental and/or systematic errors. Analytical results which differ from each other to a greater or lesser extent are generally produced not only when measurements are repeated on the same analytical sample using the same analytical method but also, to an even greater extent, if different analytical methods are used. If, however, two different methods are to be used optionally, steps shall be taken to ensure that, with a specified sample matrix, they yield equivalent analytical results.

The purpose of this standard is to verify the equivalence of two different analytical methods using statistical methods.

**3 Concepts, quantities and symbols****3.1 Concepts****3.1.1 Equivalence**

Two analytical methods are considered equivalent if, when determining a specific parameter of an analytical sample, the results obtained using one analytical method do not differ from those obtained using the other method.

Note. On the other hand, if the equivalence of two analytical methods is to be verified by comparing the results of examining different samples using different matrices, a different procedure shall be employed (cf. [1]).

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### 3.1.2 Reference method

Reference method is an analytical method required by a regulation (e.g. law, ordinance) for determining a particular parameter. As a rule, this is a standard method.

### 3.1.3 Comparison method

Comparison method is an analytical method which is to be verified for equivalence with the reference method.

## 3.2 Quantities and symbols

<i>AV</i>	analytical method
<i>R</i>	reference method
<i>V</i>	comparison method
<i>TV</i>	test value (in the German-language version denoted as PW)
$s_{x0}$	standard deviation of the method
<i>f</i>	number of degrees of freedom
<i>P</i>	probability, in %
<i>N</i>	number of analyses used for calibration
$F_{1R, fV, P}$	tabular value of the <i>F</i> -distribution with $f_1 = f_V$ and $f_2 = f_R$ (degrees of freedom for <i>P</i> %).

## 4 Designation

Designation of the method of determining the equivalence of two analytical methods by comparing the results obtained with an identical sample (A 71):

Method DIN 38402 – A 71

## 5 Procedure

### 5.1 General

To obtain equivalent analytical results using two different methods, care shall be taken to ensure that the two methods have the same statistical characteristics. The standard deviation of the comparison method,  $s_{x0V}$  (determined as specified in DIN 38402 Part 51), shall not differ in a statistically significant manner from the standard deviation of the reference method,  $s_{x0R}$ , or it shall be less than  $s_{x0R}$ . In addition, the working ranges required for the application of both methods at a later date shall coincide completely. Verification of equivalence shall be carried out for:

- the calibration characteristics of both methods determined using matrix-free samples, and
- the analytical results on actual samples to include matrix effects.

See figure 1 for a flow diagram illustrating the procedure to be followed in the verification of equivalence.

For the verification, the following samples are required:

- 5 to 10 calibration solutions as specified in DIN 38402 Part 51 (see note).
- An actual sample whose concentration shall be in the centre of the chosen working range of the calibration curve. The sample volume shall be sufficient for 50 to 100 examinations (see note). Depending on the

problems involved, it is recommended to perform the verification using several samples of different concentrations covering the chosen working range.

Note. The number of parallel determinations necessary depends on the accuracy required in the individual case. However, not less than 5 parallel determinations shall be carried out.

### 5.2 Procedure for determining statistical characteristics

#### 5.2.1 Comparison of performance characteristics of analytical methods

After a matrix-free calibration has been performed for both methods as specified in DIN 38402 Part 51 and the performance characteristics have been obtained, a performance comparison shall be made using the standard deviations of the methods,  $s_{x0}$  [1].

The test value shall be calculated from the two standard deviations of the methods,  $s_{x0V}$  and  $s_{x0R}$ , using the following equation:

$$TW = \frac{(s_{x0V})^2}{(s_{x0R})^2} \text{ for } s_{x0V} > s_{x0R} \quad (F \text{ test})$$

with the degrees of freedom  $f_R = N - 2$  and  $f_V = N - 2$ . (If  $(s_{x0V})^2 \leq (s_{x0R})^2$ , this test is unnecessary).

If the test value, *TV*, is less than or equal to the tabular value of the *F*-distribution (see table 1) ( $f_V, f_R, P = 99\%$ ) (see also DIN 38402 Part 42),  $s_{x0V}$  is not significantly greater than  $s_{x0R}$ . If the test value is greater than the tabular value of the *F*-distribution,  $s_{x0V}$  is significantly greater than  $s_{x0R}$ ; in this case, all the other tests shall only be carried out in exceptional cases.

#### 5.2.2 Verification of analytical methods

After the required number, *N*, of repeat analyses (with *N* between 5 and 10) has been made, the following analyses shall be carried out *N* times on each sample [1]:

- reference method, to be evaluated using the calibration function;
- reference method, using the standard addition method;
- comparison method, to be evaluated using the calibration function;
- comparison method, using the standard addition method.

If one of the four variants, a) to d), cannot be employed for technical reasons (e.g. if evaluation using a calibration function does not form part of the reference method), the following series of measurements shall be made as a simplified procedure for verifying equivalence [2], [3]:

- The actual sample shall be analyzed 5 to 10 times by the following procedure specified for the reference method.
- The actual sample shall be analyzed 5 to 10 times by the following procedure specified for the comparison method.

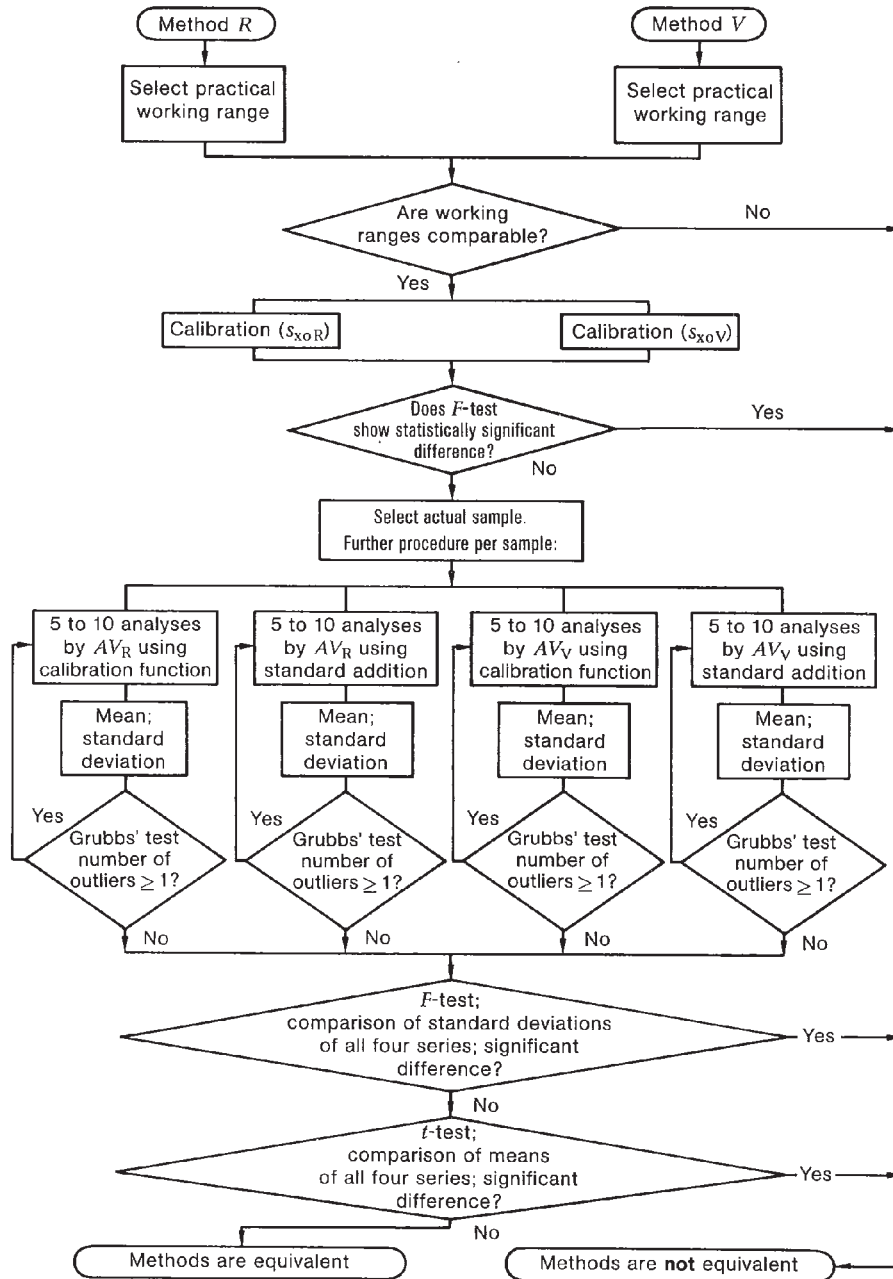


Figure 1. Flow diagram illustrating the procedure to be followed in the verification of equivalence