

Algorithms and number formats for Metrohm titration instruments

Introduction

This document explains some of the algorithms and number formats used in the instrument software. It applies to the following Titrino instruments:

Titrimo 701, 702, 716, 718, 719, 736, 751, 758, 784, 785, 787, 794, 795, 798, 799

KF Coulometer 737, 756, 831 **Titroprocessor** 726, 796

Number format

In the Titrino software the Standard **IEEE 754** (1985) for binary floating-point arithmetic has been implemented as "single precision" (32 Bit).

Rounding method

Measured values and results are displayed rounded, depending on user settings. For that purpose, arithmetic rounding is carried out according to the following method:

Example for rounding to $n = 3$ decimal places:

- 1.) $99.644499 \xrightarrow{\cdot 10^n} 99644.499$
- 2.) $99644.499 \xrightarrow{+0.5} 99644.999$
- 3.) $99644.499 \xrightarrow{cut} 99644$
- 4.) $99644 \xrightarrow{\cdot 10^{-n}} 99.644$

Statistics

The arithmetic mean value as well as the absolute and relative standard deviations for the results RS, endpoints EP and variables C are calculated:

Mean value

$MN_k \{MN_1, \dots, MN_9\}$ of results $RS_{i,j}$ each with n individual results $\{RS_{1,1}, \dots, RS_{9,20}\}$:

$$MN_k = \frac{1}{n} \cdot \sum_{i=1}^n RS_{1,i}$$

Absolute standard deviation

$Sabs_k \{Sa_1, \dots, Sa_9\}$ of results $RS_{i,j}$ each with n individual results $\{RS_{1,1}, \dots, RS_{9,20}\}$:

$$Sabs_k = + \sqrt{\frac{\sum_{i=1}^n (RS_{1,i} - MN_k)^2}{n-1}}$$

Relative standard deviation (in %)

$Srel_k \{Sr_1, \dots, Sr_9\}$ of results $RS_{i,j}$ each with n individual results $\{RS_{1,1}, \dots, RS_{9,20}\}$:

$$Srel_k = + \sqrt{\frac{\sum_{i=1}^n (RS_{1,i} - MN_k)^2}{n-1}} \cdot \frac{100}{MN_k}$$

The individual values with the number of significant digits as defined by the user are used in the calculation; they are also given out individually in the same way.

Explanation

The statistical calculations in the software have been implemented in such a way that they are as revisable as possible for the user. This is why the individual values used in the statistics are in the rounded presentation form selected by the user.

It is not the number of decimal places which is decisive for the accuracy of the calculations, but rather the number of significant digits of the decimal numbers used. As a result of the binary 32-Bit number format implemented on the basis of the IEEE 754 Standard, the decimal numbers which are produced have 7 reliable significant digits.

You can influence the number of significant digits by selecting the unit and the number of decimal places. As the results unit to be set sometimes contains both the prefix 'milli' and also the physical unit itself, the number of significant digits is altered accordingly in such a case by 3 places.

Example

The displayed result 1234.56789 mg/L has 7 reliable digits. It is to be rounded to three decimal places according to the rounding method given above:

1234.568 mg/L (7 significant digits, 3 of which are decimal places)

With the unit 'g/L' the same result 1.23456789 g/L is also rounded to three decimal places:

1.235 g/L (4 significant digits, 3 of which are decimal places)

The number of significant digits has now been reduced by three by omitting the prefix 'milli'.

You will obtain the smallest loss of rounding accuracy by selecting the application and number format so that the displayed numbers contain as many pre-decimal places as possible.

A complete recalculation of the statistics using a pocket calculator or a PC calculation program can produce variations. This is caused by the different binary number formats used in these instruments. Whereas the described titration instruments calculate with binary 32 Bit numbers as described above, PC programs (e.g. MS-Excel) use a different binary format, e.g. 64 Bit.

Conclusion

The losses of accuracy by rounding described above in the range of the maximum reliable digits are only theoretically relevant. For example, they are lower by several orders of magnitude than the uncertainties resulting from weighing out the sample.