# BASIC CHEMOMETRIC EVALUATION

Arithmetic mean $\overline{x}$ **:**

$$\overline{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

*where: n* …number of parallel analyses,

$x_i$ ….measured values.

Parameter estimation $\sigma$ is standard deviation SD, *s*. The precision calculated for $n \geq 10$ according follow:

$$s = \sqrt{\frac{1}{(n-1)}\sum_{i=1}^{n}(x_i - \overline{x})^2}$$

For $n \leq 10$, calculated according to *Dean and Dixon* with variation range *R*:

$$s_R = k_n \cdot R$$

$$R = x_{\max} - x_{\min}$$

*where:* $k_n$ … Dean-Dixon's coefficient for *n* measurements (values in table S.1),

$x_{\max}$ …the heights (maximum) value in their ascending order.

$x_{\min}$ ....the lowest (minimum) one.

*Tab. S.1: Dean-Dixon's coefficient* $k_n$

| n | $k_n$ | n | $k_n$ |
|---|---|---|---|
| 2 | 0.8862 | 7 | 0.3698 |
| 3 | 0.5908 | 8 | 0.3512 |
| 4 | 0.4857 | 9 | 0.3367 |
| 5 | 0.4299 | 10 | 0.3249 |
| 6 | 0.3946 | | |

*Relative standard deviation (RSD):*

$$s_r = \frac{s}{\overline{x}} \cdot 100 \quad [\%]$$

The confidence interval is interval in which is the value with predetermined probability 1 – $\alpha$, if the method is not affected by systematic error. Confidence level 1 – $\alpha$ is most often 0.95.

For $n \geq 10$, the *confidence interval* $L_{2,1}$ the following:

$$L_{2,1} = \bar{x} \pm s \frac{t_{\alpha/2(v)}}{\sqrt{n}}$$

*where:* $t_{\alpha/2}(v)$ is critical value of Student's distribution for selected value $\alpha$ and number of degrees of freedom $v = n - 1$ (in table S.2).

*Tab. S.2: Critical values of Student's distribution* $t_{\alpha/2}(v)$

| ν | α | | | | ν | α | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0.1 | 0.05 | 0.039 | 0.01 | | 0.1 | 0.05 | 0.039 | 0.01 |
| 1 | 6.314 | 12.706 | 16.303 | 63.657 | 16 | 1.746 | 2.120 | 2.248 | 2.921 |
| 2 | 2.920 | 4.303 | 4.914 | 9.925 | 17 | 1.740 | 2.110 | 2.237 | 2.898 |
| 3 | 2.353 | 3.182 | 3.517 | 5.841 | 18 | 1.734 | 2.101 | 2.226 | 2.878 |
| 4 | 2.132 | 2.776 | 3.024 | 4.604 | 19 | 1.729 | 2.093 | 2.217 | 2.861 |
| 5 | 2.045 | 2.571 | 2.778 | 4.032 | 20 | 1.725 | 2.086 | 2.209 | 2.845 |
| 6 | 1.943 | 2.447 | 2.631 | 3.707 | 25 | 1.708 | 2.060 | 2.178 | 2.787 |
| 7 | 1.895 | 2.365 | 2.534 | 3.499 | 30 | 1.697 | 2.042 | 2.159 | 2.750 |
| 8 | 1.860 | 2.306 | 2.465 | 3.355 | 40 | 1.684 | 2.021 | 2.134 | 2.704 |
| 9 | 1.833 | 2.262 | 2.414 | 3.250 | 50 | 1.676 | 2.008 | 2.120 | 2.678 |
| 10 | 1.812 | 2.228 | 2.374 | 3.169 | 60 | 1.671 | 2.000 | 2.210 | 2.668 |
| 11 | 1.796 | 2.201 | 2.342 | 3.106 | 80 | 1.664 | 1.990 | 2.099 | 2.639 |
| 12 | 1.782 | 2.179 | 2.317 | 3.055 | 100 | 1.660 | 1.984 | 2.092 | 2.626 |
| 13 | 1.771 | 2.160 | 2.295 | 3.012 | 200 | 1.652 | 1.972 | 2.078 | 2.606 |
| 14 | 1.761 | 2.145 | 2.277 | 2.977 | ∞ | 1.645 | 1.960 | 2.066 | 2.576 |
| 15 | 1.753 | 2.131 | 2.262 | 2.947 | | | | | |

For $n \leq 10$, the *confidence interval* $L_{2,1}$ is according *Dean and Dixon:*

$$L_{2,1} = \bar{x} \pm K_n^{\alpha} \cdot R$$

*where:* $K_n^{\alpha}$ ... Dean-Dixon's ccoefficient for pro for selected value $\alpha$ and number of measurements $n$ (values in table S.3).

*Tab. S.3: Values of Dean-Dixon's ccoefficient* $K_n^{\alpha}$

| n | (1-α) | | n | (1-α) | |
|---|---|---|---|---|---|
| | 0.95 | 0.99 | | 0.95 | 0.99 |
| 2 | 6.40 | 31.80 | 7 | 0.33 | 0.51 |
| 3 | 1.30 | 3.01 | 8 | 0.29 | 0.43 |
| 4 | 0.72 | 1.32 | 9 | 0.26 | 0.37 |
| 5 | 0.51 | 0.84 | 10 | 0.23 | 0.33 |
| 6 | 0.40 | 0.63 | | | |

## 2.2. The outlier test

The Grubbs (T-test) or Dean-Dixon's test are used in practice. The tests eliminate the outlier values from results.

The testing is performed for the highest ($x_n$) and lowest ($x_1$) value of results ordered in ascending order by size.

*Grubbs test*:

$$T_n = \frac{|\bar{x} - x_n|}{s_n}. \qquad T_1 = \frac{|\bar{x} - x_1|}{s_n}$$

$$s_n = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^2}$$

Calculated values $T_n$ and $T_1$ are confirmed with tabulated critical values $T_n^{\alpha}$. If is $T_n \geq T_n^{\alpha}$, *or* $T_1 \geq T_n^{\alpha}$., the highest, or lowest results outlier. In this case, we must eliminate this value from results and the next evaluation carries out without it. The tabulated critical values $T_n^{\alpha}$ are in table S.4.

*Tab. S.4*: *Critical tabulated values of* $T_n^{\alpha}$

| n | α | | | | n | α | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0.01 | 0.025 | 0.05 | 0.1 | | 0.01 | 0.025 | 0.05 | 0.1 |
| 3 | 1.414 | 1.414 | 1.412 | 1.406 | 12 | 2.663 | 2.519 | 2.387 | 2.229 |
| 4 | 1.723 | 1.710 | 1.689 | 1.545 | 13 | 2.714 | 2.562 | 2.426 | 2.264 |
| 5 | 1.955 | 1.917 | 1.869 | 1.791 | 14 | 2.759 | 2.602 | 2.461 | 2.297 |
| 6 | 2.130 | 2.067 | 1.996 | 1.894 | 15 | 2.800 | 2.638 | 2.493 | 2.326 |
| 7 | 2.265 | 2.182 | 2.093 | 1.974 | 16 | 2.837 | 2.670 | 2.523 | 2.354 |
| 8 | 2.374 | 2.273 | 2.172 | 2.041 | 17 | 2.871 | 2.701 | 2.551 | 2.380 |
| 9 | 2.464 | 2.349 | 2.237 | 2.097 | 18 | 2.903 | 2.728 | 2.577 | 2.404 |
| 10 | 2.540 | 2.414 | 2.294 | 2.146 | 19 | 2.932 | 2.754 | 2.600 | 2.426 |
| 11 | 2.606 | 2.470 | 2.343 | 2.190 | 20 | 2.959 | 2.778 | 2.623 | 2.447 |

For numbers of measurements, $n$ = 3–10, the outlier test for extreme values can be perform according *Dean-Dixon's test*. All three values must be to each other different!:

$$Q_n = \frac{x_n - x_{n-1}}{R}, \qquad Q_1 = \frac{x_2 - x_1}{R}$$

Calculated values $Q_n$ and $Q_1$ are confirmed with tabulated critical values $Q_n^{\alpha}$. If is $Q_n \geq Q_n^{\alpha}$, *or* $Q_1 \geq Q_n^{\alpha}$, the highest, or lowest results outlier. In this case, we must eliminate this value from results and the next evaluation carries out without it. The tabulated critical values $Q_n^{\alpha}$ are in table S.5.

*Tab. S.5: Critical tabulated values of* $Q_n^{\alpha}$

| n | α | | | | n | α | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0.01 | 0.025 | 0.05 | 0.1 | | 0.01 | 0.025 | 0.05 | 0.1 |
| 3 | 0.886 | 0.941 | 0.972 | 0.988 | 7 | 0.434 | 0.507 | 0.586 | 0.637 |
| 4 | 0.679 | 0.765 | 0.846 | 0.889 | 8 | 0.399 | 0.468 | 0.543 | 0.590 |
| 5 | 0.557 | 0.642 | 0.729 | 0.760 | 9 | 0.370 | 0.437 | 0.510 | 0.555 |
| 6 | 0.482 | 0.560 | 0.644 | 0.698 | 10 | 0.349 | 0.412 | 0.483 | 0.527 |