Polarography

1. Introduction

Polarography is an electroanalytical technique that measures the current flowing between two electrodes in the solution (in the presence of gradually increasing applied voltage) to determine the concentration of solute and its nature respectively. It is a type of voltammetry where the working electrode is a dropping mercury electrode (DME) or a static mercury drop electrode (SMDE), which are useful because they have a wide cathodic range and renewable surface.

Voltammetry is a category of electroanalytical methods where the information about the analyte is obtained by measuring current as the potential is varied. The analytical data for a voltammetric experiment is depicted in the form of a voltammogram (a polarogram in case of polarography) which plots the current produced by the electrolyte vs. the potential of the working electrode.

The current flowing through the working electrode is made up of two components:

1. Faradic Current \( (i_F) \) which is based on the oxidation and reduction of the analyte and contributes to the useful signal.

2. Capacitive Current \( (i_C) \) which is generated by charging and discharging of the electrochemical double layer on the surface of the working electrode and contributes to the unwanted interference component (noise) in the signal.

In the simplest case of Direct Current Polarography (DCP), a constant potential is applied during the entire drop-life time. A current-voltage curve is constructed by applying a series of potential steps when each step is synchronized with the drop fall. The current is measured at the end of the drop life. The sensitivity of DCP experiments is limited by the ratio of \( i_F/i_C \) (also known as a signal to noise ratio). Polarographic determinations with higher sensitivity are only possible if the ratio \( i_F/i_C \) can be improved by other measuring techniques (by increasing \( i_F \) or by reducing \( i_C \)).

**Sampled DC Polarography** and **Pulsed Methods** (Square Wave Polarography (SWP), Normal Pulse Polarography (NPP), Differential Pulse Polarography (DPP)) aim at (partial) elimination of capacitive current \( (i_C) \), whereas Stripping Voltammetry aim is to increase the faradic current \( (i_F) \).
2. Three Electrode Setup

Voltammetry is the study of current as a function of applied potential. These curves \( I = f(E) \) are called voltammogram. The potential is varied arbitrarily either step by step or continuously, and the actual current value is measured as the dependent variable. Most experiments control the potential (volts) of an electrode in contact with the analyte while measuring the resulting current (amperes).

To conduct such an experiment, one requires at least two electrodes. The working electrode, which makes contact with the analyte, must apply the desired potential in a controlled way and facilitate the transfer of charge to and from the analyte. A second electrode acts as the other half of the cell. This second electrode must have a known potential with which to gauge the potential of the working electrode. Furthermore, it must balance the charge added or removed by the working electrode. While this is a viable setup, it has some shortcomings. Most significantly, it is challenging for an electrode to maintain a constant potential while passing current to counter redox events at the working electrode.

To solve this problem, the roles of supplying electrons and providing a reference potential are divided between two separate electrodes. The Reference Electrode (RE) is a half cell with a known reduction potential. Its only role is to act as a reference in measuring and controlling the working electrode's potential and at no point does it pass any current. The Auxiliary/Counter Electrode (AE/CE) passes all the current needed to balance the current observed at the working electrode. To achieve this current, the auxiliary will often swing to extreme potentials at the edges of the solvent window, where it oxidizes or reduces the solvent or supporting electrolyte. These electrodes, working, reference, and auxiliary make up the modern three electrode system.

![Diagram of a three-electrode setup](image)

**Figure 1.** Scheme of the three-electrode setup: (1) working electrode; (2) counter electrode; (3) reference electrode
2.1. **Polarographic methods**

2.1.1. **Direct Current Polarography (DCP)**

In DCP a constant potential is applied during the entire drop-life time. A current-voltage curve is constructed by applying a series of potential steps, each step being synchronized with the drop fall. In most instruments, however, linearly changing potential is applied, with a rate slow enough that the change of potential throughout the drop-life time is about a few millivolts. The current is measured at the end of the drop life.

2.1.2. **Square Wave Polarography (SWP)**

In Square Wave Polarography, the current at a working electrode is measured while the potential between the working electrode and a reference electrode is swept linearly in time. The potential waveform can be viewed as a superposition of a regular square wave onto an underlying staircase.

![Figure 2. Square Wave Polarography. Excitation Signal (Left), Polarogram (Right)](image)

The current is sampled at two times - once at the end of the forward potential pulse (1) and again at the end of the reverse potential pulse (2) (in both cases immediately before the potential direction is reversed). As a result of this current sampling technique, the contribution to the current signal resulting from capacitive (sometimes referred to as non-faradaic or charging) current is minimal. As a result of having the current sampling at two different instances per square wave cycle, two current waveforms are collected - both have diagnostic value and are therefore preserved. When the difference between these two current values determined for a potential ramp is plotted against the particular potential, then a peak-shaped polarogram is obtained with the peak current and potential.

2.1.3. **Normal Pulse Polarography (NPP)**

In normal pulse polarography (NPP) the potential is not altered by a continuously increasing potential ramp, but by square wave potential pulses with increasing height (pulse amplitude $\Delta E_p$), overlaid on a constant initial potential. The mercury-drop electrode is held for
most of its duration at a constant potential $E_n$, at which no electrochemical reaction takes place under given experimental conditions. The potential of interest $E_p$ is applied in the last stage of the drop life, for a length of time $t_p$ (of the order of few milliseconds). The values of $E_n$ and $t_p$ are kept constant throughout the recording of the polarogram and $E_p$ is changed from drop to drop.

![Figure 3. Normal Pulse Polarography. Excitation Signal (Left), Polarogram (Right)](image)

The limiting current in NPP is diffusion controlled. Since $t_p$ is of the order of milliseconds, the diffusion layer thickness is minimal compared to the radius of the mercury drop reached at the end of its life. Furthermore, the area of the drop is virtually constant during the application of the pulse. As potential alteration at each drop is relatively significant and the pulse time very short, a large concentration gradient is produced and, as a result, a sizeable faradaic current. In contrast, the capacitive current remains small, as the measurement is made with the surface of the mercury drop remaining constant and $i_c$ has practically vanished at the time that the measurement is made. The measured current is recorded or stored until the next measurement (on the next drop). If the individual current values are plotted against the potential alteration of the pulse, then step-shaped current-potential curves are obtained. The curves are peak-shaped if the current of each preceding pulse is subtracted from the stored measured value of the following one.

2.1.4. Differential pulse polarography (DPP)

The most efficient pulse method is differential pulse polarography (DPP). In digital instruments, the excitation signal consists of a staircase-shaped increasing direct potential (potential step $\Delta E_s$), to which small square wave pulses with a constant potential (pulse amplitude $\Delta E_p$) are applied in periodic succession. The superimposition is synchronized with the drop time and takes place when the electrode surface no longer changes.
Figure 4. Differential Pulse Polarography. Excit. Signal (Left), Polarogram (Right)

The current is measured twice at each mercury drop, before each pulse and at the end of the pulse time \( t_p \). The difference between the measurements \( (\Delta i_p) \) is plotted against the direct potential and produces peak-shaped polarograms. The formation of this difference also leads to a further reduction of the capacitive current contribution and therefore to an increase in sensitivity, even when compared with determinations by normal pulse polarography.

2.1.5. Overview

Figure 5. Graphic overview of different potential waveform (left) together with corresponding polarograms (right)
3. Types of Mercury Electrodes Used in Polarography

In polarography, mercury is used as a working electrode, because mercury is a liquid metal and thus the electrode can be renewed after each droplet. The working electrode is often a drop suspended from the end of a capillary tube.

![Diagram of types of mercury electrodes](image)

**Figure 6. Types of Electrode used in Polarography (a) Hanging Mercury Drop Electrode (b) Dropping Mercury Electrode (c) Static Mercury Drop Electrode**

There are three types of electrodes:

1. **DME (Dropping Mercury Electrode):** The mercury drop forms at the end of the capillary through gravity. It grows continuously – as the mercury flows from the reservoir and has a finite lifetime of several seconds. It is then dislodged and replaced by a new drop.

2. **SMDE (Static Mercury Drop Electrode):** This electrode uses a solenoid plunger to control the flow of mercury. Activation of the solenoid momentarily lifts the plunger, allowing mercury to flow through the capillary and forming a single hanging Hg-drop.

3. **HDME (Hanging Mercury Drop Electrode):** The drop of mercury is extruded by rotating a micrometer screw that pushes the mercury from a reservoir through a narrow capillary.
4. Basic Statistics

4.1. Calibration

Generally, the main aim of analytical chemistry is to detect the presence of the analyte and to determine its amount (if possible). Apart from the absolute methods such as volumetric analysis or gravimetry all analytical methods require some sort of calibration. Calibration means the assignment of the dependent variable values (signal value – current, potential, absorbance, conductivity, etc.) to the independent variable values (concentration, volume, weight, etc.). The calibration includes two necessary steps. First is the construction of the regression model from the results of calibration standard analyses. The second step is the usage of the calibration model for the determination of $x$ value.

![Figure 7. Example of the calibration curve](image)

The most common and simplest calibration model is a linear regression model. Mathematically expressed as:

$$y = a \cdot x + b$$

Where $a$ is the slope and $b$ is the intercept. Both of the parameters are loaded with errors. The error value depends on the number of calibration points and the repetition variance. In the case, where the intercept is statistically non-significant is the equation reduced to:
\[ y = a \cdot x \]

### 4.1.1. Intercept Significance T-test

The t-test determines whether the coefficient \( b \) deviate significantly from the predicted value \( \beta \). Commonly, it is tested whether parameter \( b \) differs significantly from the origin:

\[
t = \frac{|b - \beta|}{s_b} = \frac{|b - 0|}{s_b} = \frac{|b|}{s_b}
\]

Where \( s_b \) is the standard deviation of the intercept defined as:

\[
s_b = s_e \cdot \sqrt{\frac{\sum_{i=1}^{n} x_i^2}{n \cdot \sum_{i=1}^{n} (x_i - \bar{x})^2}}
\]

Where \( s_e \) is a standard deviation of residues:

\[
s_e = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y})^2}{n - 2}}
\]

Where \( \sum_{i=1}^{n} (y_i - \hat{y})^2 \) is the regression sum of squares.

The result value is compared with value \( t_{crit} \) (you can obtain it using T.INV excel function) and:

- If \( t < t_{crit} \) then the hypothesis holds. Which means that the intercept is not statistically significant and the straight line goes through the origin.

- If \( t > t_{crit} \) then the hypothesis is denied that means the intercept is significant, and the straight line does not go through the origin.

The critical value of the T-test is defined as:

\[
t_{crit} = t_{1-\alpha/2, n-v}
\]

where \( \nu \) represents degrees of freedom and \( n \) is a number of points in the calibration curve. The degrees of freedom depend on the type of model equation. Generally, the equation \( \nu = n - k \) holds true. The \( k \) is a number of constants in the regression equation.

### 4.2. Result Errors

The purpose of the measurement is to determine the value of the measured quantity that characterizes the given property. By repeating the measurement, we come to a conclusion that, despite considerable precision, we do not always get the same value, but the values differ from
each other. This is due to the fact that individual measurements are loaded with various effects of noise, which are generally referred to as errors. The result of such a repeated measurement can then be expressed by an appropriate estimate of the mean $\mu$ (mean, median, …) and the degree of variance of this value (dispersion, standard deviation, expanded uncertainty, confidence interval).

![Figure 8. Graphic illustration of accurate and precise measurements](image)

Depending on the cause, we can divide the errors into three basic groups:

4.2.1. **Random Errors**

If the measurement is repeated several times, the random errors are shown with the same probability for both positive and negative values. Their size is given by the statistical distribution width of the measurement. They are caused by a variety of causes and cannot be removed. However, they can be statistically evaluated, and we can estimate the size of their contribution. Moreover, their influence on the measurement can be reduced by increasing the number of repetitions.

These errors affect the precision of the measurement; in other words the tightness of the match between repeated measurements under the same conditions. This phenomenon is generally called uncertainty ($u_c$). The uncertainty can be express in many ways; e.g., a standard deviation, an expanded uncertainty, or a confidence interval. Basic estimation of $u_c$ is the standard deviation $s$ which is defined as:

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

After, the confidence interval can be calculated:

$$ L_{1.2} = \bar{x} \pm \frac{s \cdot t_{crit}}{\sqrt{n}} = \bar{x} \pm s_{\bar{x}} \cdot t_{crit} $$
Wherein \( L_1 \) and \( L_2 \) represent the extreme limits of the confidence interval, \( t_\alpha \) is the critical value of the Student distribution for the chosen significance level \( \alpha \).

With a small number of parallel measurements \( (n << 10) \) the standard deviation can be determined from the range \( (R) \):

\[
s_R = k_n \cdot R
\]

\[
R = x_{max} - x_{min}
\]

Where \( k_n \) is a coefficient of the Dean-Dixon test. Based on this test the extreme limits of the confidence interval can be calculated:

\[
L_{1,2} = \bar{x} \pm K_{crit} \cdot R
\]

Where \( K_\alpha \) is the critical value of the Lord’s distribution for the chosen significance level \( \alpha \).

4.2.2. Systematic Errors

In the overall result, systematic errors are displayed by shifting the measured value in a comparison to the correct value. In the case of one value, we are talking about the accuracy of the measurement - the consistency of the measured value with the reference value (different technique, SRM, etc.). In the case of an average value obtained from repeated measurements, we are talking about the truthfulness of the measurement - the consistency between the average value of the infinite number of repeated measurements and the reference value. They are caused by the use of inappropriate methodology, poor calibration or interferences. They can be detected by comparing with another device or by comparing it with a reference material value. The cause can be found, and this type of error can be removed. Systematic errors can be quantified using so-called bias - the difference between the mean value of the measurement result and the reference value. Accuracy test can be done either with SD – Student’s t-test:

\[
t = \frac{|\bar{x} - \mu| \cdot \sqrt{n}}{s} = \frac{|\bar{x} - \mu|}{s_x}
\]

Alternatively, using a range for a small set – Lord's correctness test:

\[
u_0 = \frac{|\bar{x} - \mu|}{R}
\]
4.2.3. Gross Errors

This type of error is caused, by the improper recording of the measured quantity, the sudden failure of the instrument or failures in the procedure. Gross errors cause the measurement to be significantly different from the other repetitions. Gross errors thus affect both the precision and the accuracy of the measurement. A residual test can reveal these gross errors. These errors can and should be avoided with personal thoroughness during measurement and appropriate instrument maintenance.

Gross errors can be revealed with Grubb’s test:

$$T_n = \frac{|\bar{x} - x_n|}{S}$$

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

Dean-Dixon test is used for the small set again:

$$Q_n = \frac{x_n - x_{n-1}}{R}$$

Usually only the lowest and highest values are tested. If they are loaded with gross errors, the test has to be done for second lowest/highest value too.

4.3. Measurement uncertainty

Measurement uncertainty yields quantitative information about the quality of the analysis results. According to the exact definition, measurement uncertainty is the expression of the statistical dispersion of the values attributed to a measured quantity. So, the result combines two parts:

1. Measured value (mean, median, …)
2. Measurement uncertainty (standard deviation, …)

Based on this, the result is written as:

(value ± uncertainty) unit

(y ± U) unit

4.3.1. Propagation of Uncertainty

In many cases, the result of the analysis is affected by more quantities (with their own uncertainties). Due to that fact, the combined uncertainty has to be calculated.
### Mathematical Operation

<table>
<thead>
<tr>
<th>Mathematical Operation</th>
<th>Example</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Addition and Subtraction</td>
<td>$y = A + B$</td>
<td>$u_c = \sqrt{u(A)^2 + u(B)^2}$</td>
</tr>
<tr>
<td>2. Multiplication and Division</td>
<td>$y = A \cdot B$</td>
<td>$\frac{u_c}{y} = \sqrt{\left(\frac{u(A)}{A}\right)^2 + \left(\frac{u(B)}{B}\right)^2}$</td>
</tr>
<tr>
<td>3. Multiplication and Division</td>
<td>$y = A \cdot B$</td>
<td>$u_c = \sqrt{RSD(A)^2 + RSD(B)^2}$</td>
</tr>
</tbody>
</table>

The last step in the evaluation is the calculation of so-called expanded uncertainty $U$ which is a part of the final report. Expanded uncertainty is an interval in which the real value of the measured quantity lies with high reliability.

$$U = k \cdot u_c$$

Where $k$ is the coefficient of expansion, which is equal to two (for a 95 % level of reliability).

### 4.4. Equivalency of obtained results

Usually, the equivalency is considered when the comparison of the results is needed. Results might be provided by a different method, person, laboratory, etc.

For the equal number of repetitions in all tested sets of values is the Student’s t-test used:

$$t = \frac{|\bar{x}_A - \bar{x}_B| \cdot \sqrt{n - 1}}{\sqrt{s_A^2 + s_B^2}}$$

The $t$ value is compared to $t_{crit}$ and if $t \geq t_{crit}$ for the total number of repetitions $2n-1$ and the chosen level of significance, the difference of the arithmetic means is statistically significant. The same rule holds for the Lord’s test where is $u$ compared to $u_{crit}$:

$$u = \frac{|\bar{x}_A - \bar{x}_B|}{\frac{1}{R_A} + \frac{1}{R_B}}$$

### 5. Experimental Part

Check the instructions part carefully. Try to perform all required calculations before the laboratory course. Please, bring your own samples, details below.
5.1. **Turning the device on**

- First, turn the computer on (no password required) after that the instrument itself.
- Open the $\text{N}_2$ valves (one for each instrument) and set the pressure to 1.0 bar.
- Run 757 VA Computrace software (no username and password required).
- Load the method and check method specifications and all parameters.

5.2. **Switching off the devices**

After the measurements close the Computrace program. Then the polarograph is switched off and the nitrogen supply on/off button turned down. Then the computer can be shut down. The electrodes should be immersed in Milli-Q water with KCl solution. Never leave the electrodes to dry.

5.3. **Waste Disposal**

Between changing two measuring solutions, the electrodes have to be carefully rinsed with Milli-Q water. All measuring solutions containing mercury have to be disposed into the dedicated PVC container (fume hood). After that, the measuring vessel should be rinsed too. If necessary, mercury spilled mercury droplets can be collected with a special Hg-spoons.
6. Tasks

6.1. Determination of heavy metals in water samples

The aim is to quantify an amount of four metal cations (Zn$^{2+}$, Cu$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$) in three various samples using differential pulse polarography with HMDE. Quantification is performed via the standard addition method.

Please bring your own samples ($V > 500$ mL each):

1. drinking water with a known concentration of heavy metals (check the internet) without gas
2. water from a natural source (sea, lake, dam, well, pool, etc.).

6.1.1. Instructions

Buffer Preparation:

- Prepare 1000 mL acetate buffer of final pH 4.88
- Dissolve 18.014 g of acetic acid ($c = 99\%$, $M_r = 60.05$, $\rho = 1.05$ g/cm$^3$) in Milli-Q water
- Add sodium acetate ($M_r = 82.03$) so that the resulting concentration is 300 mM.

Standards Preparation:

- Prepare 50 mL of standard solutions according to required concentrations (use Milli-Q water):

  | Zn$^{2+}$ = 25 ppm | Cu$^{2+}$ = 15 ppm | Pb$^{2+}$ = 40 ppm | Cd$^{2+}$ = 2 ppm |

Measurement:

- Prepare 25 mL of measuring solution containing sample and buffer of ratio 4:1 directly in the measuring chamber.
- Carefully immerse the whole electrode system in the solution.
- Load the appropriate method and check the method parameters (number of repetitions, Hg droplet size, current settings, etc.).
- Start the measurement and follow software instruction.
- During the first measurement assign peaks to correct analyte.

Standard Addition Method:
• During every addition step add 2 µg of Pb\(^{2+}\), 0.1 µg of Cd\(^{2+}\), 0.75 µg of Cu\(^{2+}\), and 1.25 µg of Zn\(^{2+}\).

• As a blank, measure the Milli-Q water first at least five times.

  Note: Monitor the current during deposition step to be sure that the deposition is running correctly.

6.1.2. Evaluation

• Test all values on the presence of the outliers.
• Measure Milli-Q water as a blank.
• Determine the concentration of Zn\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) in natural water (sample you brought) as an expanded uncertainty.
• Determine the concentration of Zn\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) in tap water as an expanded uncertainty.
• Determine the concentration of Zn\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) in drinking water as an expanded uncertainty.
• Always test the significance of the intercept.
• Calculate and compare the sensitivity, LOD, and LOQ for each metal measured with HMDE. Discuss the differences.
• Discuss the reasons of obtained observations.
6.2. Determination of ascorbic acid in fruit juices

The aim is to determine the level of vitamin C (ascorbic acid) in various fruit juice samples (e.g., orange juice, grapefruit juice, etc.) with both an external calibration and standard addition methods. Measurements using the differential pulse polarography with static mercury dropping electrode (SMDE).

Oxidation of ascorbic acid (vitamin C) to dehydroascorbic acid can be simplified to the following equation with the standard reduction potential \( E_0 \) of 0.08 V:

\[
\text{ascorbic acid} \rightarrow \text{dehydroascorbic acid} + 2 \text{H}^+ + 2 \text{e}^-
\]

**Buffer Preparation:**
- Use the same acetate buffer as in the metal analysis experiments.

**Calibration Curve Method:**
- Prepare 250 mL of a stock solution containing ascorbic acid (2000 mg/L) and oxalic acid (1000 mg/L) in Milli-Q water.
- Dilute the stock solution to prepare calibration solutions of 50, 100, 200, 300, 500 mg/L in 50 mL volumetric flask.
- Add 1 mL of respective calibration solution and 25 mL of acetate buffer into the electrochemical cell.
- Measure all the calibration solutions and plot the calibration curve.
- At last measure all three unknown juices in the same fashion (1 mL of sample + 25 mL of acetate buffer).

**Standard Addition Method:**
- Pipette 1 mL of juice sample and 25 mL of acetate buffer into the electrochemical cell and take the measurement.
• Add 0.5 mL of 200 mg/L ascorbic acid solution in every addition step.
• Repeat the addition at least five times.
• Perform the same measurement for all three unknown juice samples.

6.2.1. Evaluation

• Test all values on the presence of the outliers.
• Determine the concentration of ascorbic acid in juice samples as an expanded uncertainty using the calibration curve method.
• Determine the concentration of ascorbic acid in juice samples as an expanded uncertainty using the standard addition method.
• Always test the significance of the intercept.
• Calculate and compare the results, sensitivity, LOD, and LOQ for each calibration method. Discuss the differences.
• Answer which method is more suitable for juice analysis.
• Discuss the differences between the obtained results and concentration provided by the manufacturer.
7. Critical values for statistical tests

Table 1. Critical values of $K_{\text{crit}}$ (Lord’s test) and $t_{\text{crit}}$ (Student’s t-test) for the elimination of outliers and accuracy.

<table>
<thead>
<tr>
<th>Number of Repetitions</th>
<th>$K_{\text{crit}}$ $\alpha = 0.05$</th>
<th>$K_{\text{crit}}$ $\alpha = 0.01$</th>
<th>$t_{\text{crit}}$ $\alpha = 0.05$</th>
<th>$t_{\text{crit}}$ $\alpha = 0.01$</th>
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<tbody>
<tr>
<td>2</td>
<td>6.353</td>
<td>31.822</td>
<td>12.706</td>
<td>63.657</td>
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<tr>
<td>3</td>
<td>1.304</td>
<td>3.008</td>
<td>4.303</td>
<td>9.925</td>
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<tr>
<td>4</td>
<td>0.717</td>
<td>1.316</td>
<td>3.182</td>
<td>5.841</td>
</tr>
<tr>
<td>5</td>
<td>0.507</td>
<td>0.843</td>
<td>2.776</td>
<td>4.604</td>
</tr>
<tr>
<td>6</td>
<td>0.399</td>
<td>0.628</td>
<td>2.571</td>
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<tr>
<td>7</td>
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Table 2. Critical values of $k_n$ coefficient.

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<th>Number of Repetitions</th>
<th>$k_n$</th>
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<tr>
<td>2</td>
<td>0.886</td>
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<td>3</td>
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<td>5</td>
<td>0.430</td>
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<td>0.395</td>
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<tr>
<td>7</td>
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<td>8</td>
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<td>9</td>
<td>0.337</td>
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<td>10</td>
<td>0.325</td>
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Table 3. Critical values of $T_k$ and $Q_k$ for the elimination of outliers.

<table>
<thead>
<tr>
<th>Number of Repetitions</th>
<th>$T_{α}$</th>
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<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$α = 0.05$</td>
<td>$α = 0.01$</td>
<td>$α = 0.05$</td>
</tr>
<tr>
<td>3</td>
<td>1.412</td>
<td>1.416</td>
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<tr>
<td>4</td>
<td>1.689</td>
<td>1.723</td>
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Table 4. Critical values of Lord’s distribution $u_{crit}$.

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