# Simultaneous Determinations for the Internal Resistance of Three Batteries. Three Analytical Methods Involved

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***Abstract*— Surprisingly or not, batteries were the primary source of electricity before the development of electric generators and electrical grids. Perhaps Voltaic pile was the first electrical battery that could continuously provide an electric current to a circuit, even if the electrochemical behavior of zinc and copper in a bimetallic arch, in contact with the electrolytes of muscle tissue were observed before. Ordinary batteries consist of one or more electrochemical cells. A cell is created by placing electrodes in an electrolyte where a chemical reaction either generates (at battery use) or uses (at battery recharging) an electric current. Here a very simple circuit has been used to provide raw data for estimating the electromotive force of a power source. The circuit has been used to measure pairs of potential versus intensity for three commercial batteries. From measured data three methods were employed to provide estimates of the internal resistance and electromotive force. The estimating of the internal resistances is discussed.**

***Keywords*— *galvanic cells; voltaic cells; chemical potential; internal resistance regression analysis***

## I. INTRODUCTION

The energy transition towards sustainability leads us to look for new sources of renewable energy (RES) as an alternative energy production. RES bring with them adaptation problems related to the intermittent nature and energy fluctuations that often increase the complexity of planning and operating the electric power network [1]. The problem of adapting the electricity storage technology to the concrete needs that allows the flexibility of the power supply system and at the same time the adaptability to fluctuating renewable energy (wind and solar) is a topic debated by many specialists [2, 3]. Among various advanced technologies, grid-scale or utility-scale battery energy storage system is receiving wide attention due to its attractive features of flexible installation, fast response, high energy efficiency, and short construction cycle [4, 5, 6].

Batteries were the first to provide electricity before the development of electric generators. Alessandro Giuseppe Antonio Anastasio Volta, Italian physicist and chemist, pioneer of electricity and power, credited as the inventor of the electric battery (or Voltaic pile, see [7]), also discoverer of methane, actually continued the studies of Luigi Galvani, who firstly observed the electrochemical behavior of zinc and copper in a bimetallic arch, in contact with the electrolytes of muscle tissue [8]. Today the electrostatic potential difference between two metals (or one metal and one electrolyte) that are in contact and are in thermodynamic equilibrium $\Delta\psi$ is named Volta potential after Alessandro Volta. It should be noted that Volta potential it cannot be measured directly by an ordinary voltmeter, which does not measure vacuum electrostatic potentials, but instead the difference in Fermi level between the two materials, a difference that is exactly zero at equilibrium. The voltaic pile then enabled a rapid series of other discoveries including the electrolysis of water [9, 10]. Continuing and expanding Volta's work, Michael Faraday made significant progress in the study of the electricity [11]. The recent changes on the energy market make us turn even more our attention to alternative sources of energy, including storage of energy in batteries [12] and hydrogen fuel cells [13].

An electrochemical cell can be created by placing electrodes in an electrolyte where a chemical reaction either uses or generates an electric current. Electrochemical cells that generate an electric current are called voltaic (from Volta) cells or galvanic (from Galvani) cells while the other electrochemical cells in which an external source of electric current is used to drive the chemical reaction that would not occur spontaneously are called electrolytic cells or of electrolysis [14].

Metal–air batteries are between fuel cells and traditional batteries. Are similar to conventional fuel cells in that their porous positive electrode structure requires a continuous and inexhaustible oxygen supply from the surrounding air as the reactant, providing thus high energy densities and have the design features of traditional batteries in which a metal is used as the negative electrode. Recent advances in Zn-air batteries has been reviewed [15].

Therefore, flexible and practical techniques are needed to predict and estimate the actual available battery capacity and states. Accurate values are not usually obtained by classical analytical methods since measurements involve simultaneous determinations of current and voltage [16].

Important battery parameters include State-of-charge and state-of-health, which are dependent on the internal resistance of the battery, which motivated our study. The internal resistance of three batteries is here simultaneously determined.

## II. MATERIAL AND METHOD

As a chemical process, a reduction (Red) is the addition of electrons to a species and oxidation (Ox) is the removal of electrons from a species. A redox (from Red-Ox) reaction is a reaction in which there is a transfer of electrons from one species to another. It is usually expressed as the difference of two reduction half reactions.

The main equations used are presented in Table I:

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TABLE I. THE EQUATIONS FOR THE REDOX PROCESSES

| No. | The form of the equation |
|---|---|
| 1. | $Ox + \nu_e e^- \rightarrow Red$ |
| 2. | $n_e(Red) = \nu_e + n_e(Ox)$ |
| 3. | $\nu_{R1} Red_1 \rightarrow \nu_{O1} Ox_1 + \nu_e e^-$<br>$\nu_{O2} Ox_2 + \nu_e e^- \rightarrow \nu_{R2} Red_2$<br>$\nu_{R1} \cdot n_e(Red_1) - \nu_{O1} \cdot n_e(Ox_1) = \nu_{R2} \cdot n_e(Red_2) - \nu_{O2} \cdot n_e(Ox_2)$ |
| *Ox* and *Red* are two forms of a same species; $(\nu_{O1}, \nu_{R1}, \nu_{O2}, \nu_{R2}, \nu_e) = 1$ express the convention to express the coefficients of the balanced reactions as coprime numbers | |

Formally, if $\nu_e$ electrons are transferred, then the corresponding reduction half-reaction is Eq. No. 1 in Table I. If $n_e(\cdot)$ is a function counting the total number of electrons, then applied to Eq. No. 1 provides Eq. No. 2 in Table I.

The reduction and oxidation are responsible for the overall reaction in a cell and are usually separated in space: reduction takes place at one electrode and oxidation takes place at the other. The same electrons released in an oxidation at one electrode (anode) travel through the external circuit and returns to the cell through the other electrode (cathode), where there they bring about reduction Eq. No. 3 in Table I.

Typical circuits for measuring the electrochemical potential include direct measurements using a potentiometer (and then the accuracy and precision depends solely on the potentiometer), indirect measurements using a Wheatstone bridge [17], and then the accuracy and precision depends solely on the potentiometer) along with a reference potential source from a standard cell [18] such as Clark cell [19]; the standard for measuring the electrochemical potential until 1911), a Weston cell [20]; the standard for measuring the electrochemical potential from 1911 until 1990) or even a Josephson junction [21], [22]; the standard for measuring the electrochemical potential from 1990) and indirect measurements from a series of measurements of potential and intensity in a working regime. In this work is considered the latter.

A simple electric circuit with a voltmeter and an ammeter (Fig. 1) is used to record pairs of potential and intensity when the potentiometer is used to vary the resistance ($R_X$) in the circuit.

It should be noted that in general case each component introduced in the circuit have its own internal resistance (Fig. 4), and thus by considering the simplified version of it we implicitly use approximations.

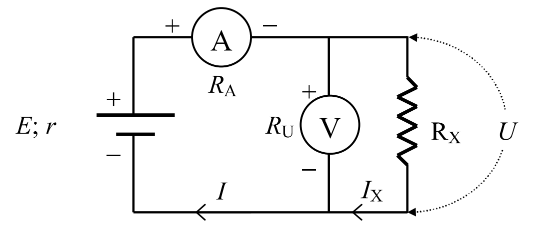

Fig. 1. Detailed circuit for measuring of electromotive force (E) and internal resistance (r)

Not neglecting the internal resistances of the instruments, the equations providing the connections between the known and unknowns are obtained from Kirchhoff's [23] laws. The system from Fig. 1 provides:

$$E = I(r + R_A) + U \tag{1}$$

where $R_U$ is the internal resistance of the voltmeter, $R_A$ the internal resistance of the ammeter, $U$ is the potential measured by the voltmeter and $I$ is the intensity measured by the ammeter.

It is clear from Eq. (1) that in order to obtain the unknowns ($E$, $r$, $R_A$) blindly use of this equation is not enough.

When the value of the potentiometer resistance ($R_X$) is subject to change the value of the potential measured by the voltmeter $U$ and of the intensity measured by the ammeter I are changing as well, and are paired thus each experimental series of measurements is a set $(I_k, U_k)_{1\le k\le n}$, where $n$ is the number of measurements.

Even so, for a series of measurements, Eq. (1) is able to provide partly the answer we seek: the values of E and of r + RA are only outcomes of a such algebraic approach. For the convenience of explaining the methods, let's consider for now the internal resistance of the ammeter incorporated into the internal resistance of the battery ($r \leftarrow r + R_A$). We will turn later on the problem of decomposing back the sum ($r \rightarrow r + R_A$). It should be noted that is no reducing of the generality or altering the outcome by doing this substitution: both $r$ and $R_A$ are constants during our experiments (r is constant for a given battery, $R_A$ is a constant for an ammeter used on the same measurement scale) and are subject to determination.

A classical approach of treatment the experimental errors would be to minim (see [24]) but here also alternate treatments (see [25]) are considered (Fig. 2).

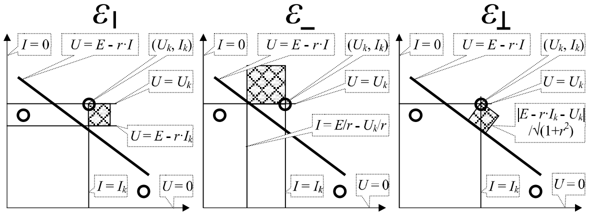

Fig. 2. Vertical ("|"), horizontal ("_") and perpendicular ("⊥") offsets in calculating of the experimental errors (ε)

Fig. 2 depicts an unitary approach for treatment of the experimental errors: in each instance the linear regression equation is the same, and the minimized squares ($S_k^2$) differs (Tab. II).

TABLE II. SOLUTIONS FOR INTERCEPT (B) AND SLOPE (A) OF THE THREE DIFFERENT APPROACHES ("|", "_", AND "⊥") MINIMIZING THE EXPERIMENTAL ERRORS (E)

| **Charac-teristics** | $\varepsilon_\vert$ | $\varepsilon_\_$ | $\varepsilon_\perp$ |
|---|---|---|---|
| Errors | $S_k^2 = (E - r \cdot I_k - U_k)^2$ | $S_k^2 = (E - r \cdot I_k - U_k)^2/r^2$ | $S_k^2 = (E - r \cdot I_k - U_k)^2/(1+r^2)$ |
| Substitutions: $y \leftarrow U$, $x \leftarrow I$; Notation: $M(\cdot)$:operator for average value from a series of values | | | |
| Slope | $a_\vert = \frac{M(x)M(y) - M(xy}{M(x)M(x) - M(xx}$ | $a_\_ = \frac{M(y)M(y) - M(yy)}{M(x)M(y) - M(xy)}$ | $c = \frac{a_\vert^{-1} - a_\_}{2}$,<br>$a_\perp = c \pm \sqrt{c^2 + 1}$ |
| Intercept | $b_\vert = M(y) - a_\vert M(x)$ | $b_\_ = M(y) - a_\_ M(x)$ | $b_\perp = M(y) - a_\perp M(x)$ |

A digital voltmeter and a digital and a analogue ammeter has been used to collect the series of the experimental data from $(I_k, U_k)_{1\leq k\leq n}$ measurements by varying the external resistance ($R_X$). Three AA-type (Alkaline) commercial batteries (produced by Energizer in Singapore under SNI 04-2051.2-2004) has been purchased form a local store and were freshly new (Tab. III).

TABLE III. BATTERIES USED IN OUR EXPERIMENT (DESIGNATION: ANSI-15A, IEC-LR6)

| **Our designation** | **Red (R)** | **Yellow (Y)** | **Blue (B)** |
|---|---|---|---|
| Image |  |  |  |
| Commercial label | MAX | Alkaline Power 1121D | MAX PLUS |
| Producer series | 12-2030 | 12-2028 | 12-2032 |
| Shelf Life | 10 years at 21 °C | 7 years at 21 °C | 10 years at 21 °C |
| Weight | 23.73969 g | 23.3814 g | 24.3389 g |
| Nominal internal resistance | 150-300 mΩ | - | - |

Note: The batteries were purchased in the same day when the experiments were conducted. One should note that extended experimental procedures may produce increase of their internal resistance.

## III. RESULTS AND DISCUSSION

The value of the potentiometer has been adjusted $n = 15$ times and in each instance $k$ the $(I_k, U_k)$ pair has been collected for each battery using the Fig. 1 circuit. Additionally, all batteries were serialized and another series of measurements were made. The results are given in Tab. IV.

TABLE IV. PAIRS OF MEASUREMENTS FOR POTENTIAL VERSUS INTENSITY FOR EACH BATTERY (R, Y, B) AS WELL AS FOR SERIALIZED CIRCUIT (RYB)

| **Nr. Crt.** | **Red (R)** | | **Yellow (Y)** | | **Blue (B)** | | **Serialized (RYB)** | |
|---|---|---|---|---|---|---|---|---|
| | ***I* (mA)** | ***U* (V)** | ***I* (mA)** | ***U* (V)** | ***I* (mA)** | ***U* (V)** | ***I* (mA)** | ***U* (V)** |
| 1 | 155.0 | 1.233 | 158.0 | 1.260 | 155.5 | 1.233 | 154.6 | 4.34 |
| 2 | 105.0 | 1.350 | 107.0 | 1.372 | 103.0 | 1.339 | 134.3 | 4.39 |
| 3 | 35.2 | 1.505 | 68.7 | 1.455 | 67.5 | 1.431 | 107.5 | 4.46 |
| 4 | 67.9 | 1.435 | 52.7 | 1.485 | 52.1 | 1.470 | 87.1 | 4.51 |
| 5 | 52.3 | 1.475 | 40.7 | 1.515 | 40.2 | 1.492 | 65.1 | 4.55 |
| 6 | 40.4 | 1.503 | 35.7 | 1.527 | 35.1 | 1.503 | 53.1 | 4.59 |
| 7 | 23.3 | 1.543 | 23.4 | 1.552 | 23.2 | 1.538 | 43.6 | 4.62 |
| 8 | 20.1 | 1.552 | 20.1 | 1.558 | 20.0 | 1.544 | 36.7 | 4.64 |
| 9 | 18.1 | 1.556 | 18.2 | 1.563 | 18.1 | 1.549 | 31.3 | 4.65 |
| 10 | 16.1 | 1.559 | 16.2 | 1.568 | 16.0 | 1.553 | 27.8 | 4.66 |
| 11 | 14.1 | 1.565 | 14.1 | 1.573 | 14.0 | 1.559 | 24.1 | 4.67 |
| 12 | 11.6 | 1.572 | 11.6 | 1.578 | 11.5 | 1.564 | 18.7 | 4.69 |
| 13 | 9.9 | 1.575 | 10.0 | 1.582 | 9.9 | 1.569 | 15.5 | 4.70 |
| 14 | 8.6 | 1.580 | 8.6 | 1.585 | 8.6 | 1.572 | 12.5 | 4.71 |
| 15 | 6.9 | 1.585 | 6.9 | 1.588 | 6.8 | 1.576 | 10.5 | 4.72 |

Three strategies for data analysis (combined with the formulas from Tab. II) were applied:

- ÷ Strategy "R": processing of the data kept intact (as in Tab. IV) and data analysis results was expressed in corresponding units (converted in Tab. V from mΩ to Ω for the internal resistance and from mV to V for electromotive force); "R" letter comes from raw data space.
- ÷ Strategy "U": processing of the data after is scaled to same units (for the electrochemical cell $I$ in μA was converted in mA and for the battery $I$ in mA was converted in A before data analysis) and data analysis results was expressed in corresponding units ($E$ is converted in Tab. V from mV to V for electromotive force after data analysis); "U" letter comes from uniform unit data space.
- ÷ Strategy "C": processing of the data scaled to [-1, 1] (a linear transformation from [min, max] to [-1, 1] was applied on each variable) before data analysis, and data analysis results were scaled back after data analysis (internal resistance is adjusted with the scaling factor, $r \leftarrow r \bullet (\max(U) - \min(U))/(\max(I)-\min(I)$; electromotive force is scaled back and shifted, $\mathrm{med}(U) \leftarrow \min(U) + (\max(U) - \min(U)) \bullet (\mathrm{med}(U) + 1)/2)$, $\mathrm{med}(I) \leftarrow \min(I) + (\max(I) - \min(I)) \bullet (\mathrm{med}(I) + 1)/2)$, $E \leftarrow \mathrm{med}(U) + r \bullet \mathrm{med}(\mathrm{I})$; "C" letter comes from contractive space, [-1, 1] × [-1, 1] being a contractive space.

The results are given in Tab. V.

TABLE V. RESULTS FROM APPLYING THE METHOD ("|", "_", "⊥") AND STRATEGY ("R", "U", "C") ON THE DATA OBTAINED FROM THE MEASUREMENTS ON THE BATTERIES ("R", "Y", "B") AND THEIR SERIALIZED SYSTEM ("RYB")

| **Battery, Method** | | **Strategy** | **Raw** | **Uniform** | **Contractive** |
|---|---|---|---|---|---|
| | | | **(R)** | **(U)** | **(C)** |
| Red (R) | Vertical offsets (\|) | $r + r_A$ | 2.368 Ω | 2.368 Ω | 2.368 Ω |
| | | $E$ | 1.598 V | 1.598 V | 1.598 V |
| | Horizontal offsets (_) | $r + r_A$ | 2.371 Ω | 2.371 Ω | 2.371 Ω |
| | | $E$ | 1.598 V | 1.598 V | 1.598 V |
| | Perpendicular offsets (⊥) | $r + r_A$ | 2.368 Ω | 2.370 Ω | 2.369 Ω |
| | | $E$ | 1.598 V | 1.598 V | 1.598 V |
| Yellow (Y) | Vertical offsets (\|) | $r + r_A$ | 2.171 Ω | 2.171 Ω | 2.171 Ω |
| | | $E$ | 1.603 V | 1.603 V | 1.603 V |
| | Horizontal offsets (_) | $r + r_A$ | 2.171 Ω | 2.171 Ω | 2.171 Ω |
| | | $E$ | 1.603 V | 1.603 V | 1.603 V |
| | Perpendicular offsets (⊥) | $r + r_A$ | 2.171 Ω | 2.171 Ω | 2.171 Ω |
| | | $E$ | 1.603 V | 1.603 V | 1.603 V |
| Blue (B) | Vertical offsets (\|) | $r + r_A$ | 2.347 Ω | 2.347 Ω | 2.347 Ω |
| | | $E$ | 1.590 V | 1.590 V | 1.590 V |
| | Horizontal offsets (_) | $r + r_A$ | 2.351 Ω | 2.351 Ω | 2.351 Ω |
| | | $E$ | 1.591 V | 1.591 V | 1.591 V |

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| Battery, Method \ Strategy | | | Raw | Uniform | Contractive |
|---|---|---|---|---|---|
| | | | (R) | (U) | (C) |
| | Perpendicular offsets (⊥) | $r + r_{\mathrm{A}}$ | 2.347 Ω | 2.350 Ω | 2.349 Ω |
| | | $E$ | 1.590 V | 1.591 V | 1.591 V |
| Serialized (RYB) | Vertical offsets (\|) | $r + r_{\mathrm{A}}$ | 2.593 Ω | 2.593 Ω | 2.593 Ω |
| | | $E$ | 4.736 V | 4.736 V | 4.736 V |
| | Horizontal offsets (_) | $r + r_{\mathrm{A}}$ | 2.602 Ω | 2.602 Ω | 2.602 Ω |
| | | $E$ | 4.736 V | 4.736 V | 4.736 V |
| | Perpendicular offsets (⊥) | $r + r_{\mathrm{A}}$ | 2.593 Ω | 2.601 Ω | 2.597 Ω |
| | | $E$ | 4.736 V | 4.736 V | 4.736 V |

Of interest, as stated in the purpose of the study, is the estimation of the internal resistance of each battery. By serializing the batteries the internal resistance of the serialized system is the sum of the internal resistance of each battery, and therefore, by subtracting from the sum of the resistances obtained for each battery (entries $r + r_{\mathrm{A}}$ for R, Y and B in Tab. V) the resistance obtained for the serialized system (entries $r + r_{\mathrm{A}}$ for RYB in Tab. IV), the value of the internal resistance of the ammeter ($r_{\mathrm{A}}$) can be obtained (Eq. (2)):

$$r_I = ½[(r_{\mathrm{R}} + r_{\mathrm{A}}) + (r_{\mathrm{Y}} + r_{\mathrm{A}}) + (r_{\mathrm{B}} + r_{\mathrm{A}}) - (r_{\mathrm{R}} + r_{\mathrm{Y}} + (r_{\mathrm{B}} + r_{\mathrm{A}})] \tag{2}$$

Now, by turning back to the $r + r_{\mathrm{A}}$ values from Tab. 4, the internal resistances of the batteries are to be obtained by a simple subtraction (Eq. (3)).

$$r_{\mathrm{R}} = (r_{\mathrm{R}} + r_{\mathrm{A}}) - r_{\mathrm{A}}\ r_{\mathrm{Y}} = (r_{\mathrm{Y}} + r_{\mathrm{A}}) - r_{\mathrm{A}},\ r_{\mathrm{B}} = (r_{\mathrm{B}} + r_{\mathrm{A}}) - r_{\mathrm{A}} \tag{3}$$

Results of applying Eq. (2) and (3) on Tab. V are given in Tab. VI.

TABLE VI. DIFFERENT ESTIMATIONS FOR THE INTERNAL RESISTANCES

| Device | Method | Value | R | U | C |
|---|---|---|---|---|---|
| Ammeter (A) | _ | $r_{\mathrm{A},\_}$ | 2.146 | 2.146 | 2.146 |
| | ⊥ | $r_{\mathrm{A},\perp}$ | 2.147 | 2.146 | 2.146 |
| | \| | $r_{\mathrm{A},\vert}$ | 2.147 | 2.147 | 2.147 |
| Red battery (R) | _ | $r_{\mathrm{R},}$ | 0.225 | 0.225 | 0.225 |
| | ⊥ | $r_{\mathrm{R},\perp}$ | 0.222 | 0.225 | 0.223 |
| | \| | $r_{\mathrm{R},\vert}$ | 0.222 | 0.222 | 0.222 |
| Yellow battery (Y) | _ | $r_{\mathrm{Y},\_}$ | 0.026 | 0.026 | 0.026 |
| | ⊥ | $r_{\mathrm{Y},\perp}$ | 0.024 | 0.026 | 0.025 |
| | \| | $r_{\mathrm{Y},\vert}$ | 0.024 | 0.024 | 0.024 |
| Blue battery (B) | _ | $r_{\mathrm{B},}$ | 0.205 | 0.205 | 0.205 |
| | ⊥ | $r_{\mathrm{B},\perp}$ | 0.201 | 0.205 | 0.203 |
| | \| | $r_{\mathrm{B},\vert}$ | 0.201 | 0.201 | 0.201 |

The values given in Tab. VI opens a series of discussions:

÷ taking now a look to the Eq. (1) we can see how the common belief that $r_{\mathrm{A}}$ is small and can be neglected is destroyed, since the values in Tab. VI shows that $r_{\mathrm{A}}$ is about 10 times greater than any battery internal resistance.

÷ a small amount of variation in the result of the estimation of the internal resistance is due to the choosing of the method of calculation and (almost, at the level of precision of our calculation) none due to the choosing of the strategy of pre-processing.

÷ the value of the internal resistance of the Red battery is in the prescript producer range ("Nominal internal resistance" in Tab. III).

÷ the higher potential and higher intensity provided by the Yellow battery (values of I and U are slightly higher for Yellow battery than for Red and Blue batteries in Table IV) is readily explained by its significantly reduced internal resistance (about ten times smaller, see Tab. VI). We should notice that this result also correlates with an reduced shelf life (see Tab. III).

÷ there is a rule in the values for the perpendicular offsets ("_" in Tab. VI) saying that the values obtained for perpendicular offsets should be expected as intermediary between the values obtained for horizontal ("_" in Tab. VI) and for vertical ("|" in Tab. VI) offsets, and even the decomposition of the sums of the internal resistances didn't changed this rule (the values listed in Tab. V obeys the rule as well).

÷ when the measurements are properly made and in the tolerance range of the instrumentation used then there are no gross or systematic errors and the expectance is to have relative close values provided by the three methods; for a method identifying extreme values - which are possible gross errors - please see [26].

## IV. CONCLUSIONS

It has been shown that the internal resistance of the meter used for measurement influences greatly the value of the estimation of the internal resistance in the case of the commercial batteries, with low internal resistance. The method used for the statistical treatment of the data have influence on the values of the internal resistance. In all considered instances, perpendicular offsets method provided corrections to the regression coefficients (which are ones and the same with internal resistance and electromotive force) balancing the errors from both voltmeter and ammeter measurements and when applied on contractive space ([-1, 1] × [-1, 1]) of transformed data provided even more balanced results. Adopting of the perpendicular offsets as a standard method for this sort of paired measurements treatment is therefore recommended.

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