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Uncertainty of Multipoint Calibration of pH-meters with Glass Electrode Used for Routine pH Measurements in the pH-mode

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ABSTRACT: Routine pH measurements are performed on daily basis in thousands of analytical laboratories around the world using pH- meters. In the literature, there is no published procedure to estimate the uncertainty of multipoint calibration of pH-meters with glass electrodes in the pH-mode. Therefore, the aim was to develop an uncertainty procedure based on ISO GUM using CRM buffer solutions of pH 4, 7 and 10 produced by an NMI signatory to the CIPM MRA. The calibration results were obtained within the uncertainty limits of the CRMs to ensure traceability of measurements. A mathematical model of the calibration function was defined and sources of uncertainty were identified and quantified. The expanded uncertainty was calculated at a confidence level of 95% by multiplying the combined standard uncertainty, u_c by a coverage factor $k=2$. This procedure will be useful for the analytical laboratories performing routine pH measurements using pH-meters in the pH-mode.

KEYWORDS: pH–meter-glass electrode-pH mode-CRM pH-multipoint calibration-uncertainty

I.INTRODUCTION

The concept of pH is unique among the commonly encountered physicochemical quantities and has been introduced early last century by S. Sorensen [1]. Measurements of pH have and still gaining great attention since decades because of its fundamental importance in judging the quality of drinking water, beverages, medicines, ground water, wastewater and others [2]. The pH measurements are also very important in biological applications and in environmental monitoring of water in rivers, lakes, seas and oceans [3,4]. In terms of its definition as: pH = −lg aH, it involves a single ion quantity, which is activity of the hydrogen ion. It is immeasurable by any thermodynamically valid method and requires a convention for its evaluation [5]. The accuracy of pH measurements remains an essential requirement in health care and safety, biochemistry and environmental monitoring [6]. One of the key controlling factors of the quality of these pH measurements is to estimate an elaborate and logical uncertainty budget to help users of the testing results make right decisions. ISO/IEC 17025 requires testing and calibration laboratories to estimate uncertainty of their measurement results taking into consideration all sources [11]. A literature survey was carried out to see what was published about the routine pH measurements carried out daily by thousands of analytical chemistry laboratories around the world using pH-meters. It has been found that a large number of articles have addressed issues of pH measurements, traceability and uncertainty [12-15]. However, articles about uncertainty have dealt with it on the high level pH measurements in the mV mode [16-18]. No published papers were found about uncertainty of the multipoint calibration of pH-meters in the pH-mode. Therefore, the aim of this article is to develop a method based on ISO GUM and EURCHEM/CITAC guide for estimation of uncertainty of multipoint calibration of pH-meters with glass electrodes in the pH mode using certified buffer standards of pH 4, 7 and 10 at 25°C [7,19]. A mathematical model of the measurement was written and sources of uncertainty were identified and quantified then the expanded uncertainty was estimated using a coverage factor $k=2$ to provide confidence level at 95% as required by ISO GUM [19]. This procedure is deemed very useful for analytical chemistry laboratories.

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II.EXPERIMENTAL

2.1. The pH-meter
The pH-meter used was of the type Mittler Toledo seven compact pH/ion S220, Switzerland. Its digital display shows a resolution of 0.001 units in the pH measurement mode. A multipoint calibration of this pH-meter can be carried out using one buffer series out of the five series stored in the memory of the meter at different temperatures. The temperature sensor was connected to the meter and thus it can automatically correct the pH. The error limits of the meter in the pH-mode is ±0.01 pH units.

2.2. The electrode system
The electrode used in this study was a combined glass electrode of the type InLab sensor pH electrode manufactured by Mittler Toledo, Switzerland. Its reference electrode is Ag/AgCl in 4 mol/L KCl solution with porous liquid junction and has a built-in temperature sensor.

2.3. Temperature control
A water bath with calibrated thermostat was used to maintain the calibration standards at 25±0.2°C during calibration and measurements.

2.4. The calibration standards
Calibration was carried out using certified buffer solutions as calibration standards produced by the Slovak National Metrology Institute (SMU) of pH 3.999±0.02, 7.006±0.02 and 9.998±0.02 at 25 °C. Thus the traceability of our pH measurement results were to the primary procedure for the measurement of pH described in IUPAC recommendation, 2002, which is adopted at SMU to produce the primary pH standard buffer solutions [2,5,6].

2.5. Calibration
The calibration of pH-meter was performed in the pH-mode using instructions of the manufacturer of pH-meter as recommended by ASTM D: E70 − 19 [20]. Together with these instructions, we have used the general calibration procedure laid down in the Thermo Technical Note [21]. In this procedure the electrode was prepared for measurements by immersion in a solution of 20 mL buffer of pH 7 and 0.1 g of KCl then rinsed with ultrapure water then with the measured buffer. All buffers were kept at 25±0.2 °C. Before calibration each buffer CRM was stirred to mix it well and both calibration and measurements were performed without stirring. Calibration was started with pH 9.998 then pH 7.006 and finally pH 9.998. To move from one buffer to the next, the electrode was rinsed with ultrapure water then with the measured buffer and dried well before immersion. The calibration was verified by measuring each CRM pH 10 times at 25°C.

III.RESULTS AND DISCUSSION

A multipoint calibration of the above described pH-meter was carried out in the pH-mode using three standard buffer solutions of pH 3.999, 7.006 and 9.998 with uncertainty of ±0.02 pH unit. The response pH calibration indications were exactly the same as the certified values mentioned above and the results were saved. The calibration was then verified by measuring each CRM 10 times within the temperature limits (25±0.2 °C) and the results obtained were reported in Table 1. The ten measurement results of each verified pH calibration were plotted within the uncertainty limits associated with each certified pH value in order to ensure the quality of the calibration results. Figures 1(b) and 2 (c, d) show these plots, from which it can be clearly seen that all

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the calibration results lie within the uncertainty limits of each CRM.

Table 1: The calibration results of pH-meter at 25 °C in the pH-mode

	pH 3.999	Temp °C	pH 7.006	Temp °C	pH 9.998	Temp °C
	3.995	25.1	6.993	25.1	9.991	25.0
	3.989	25.0	6.989	25.0	10.004	25.1
	3.999	24.9	7.002	24.9	9.998	24.9
	3.995	25.0	7.002	24.8	10.003	25.1
	3.997	24.9	7.005	25.0	9.987	25.9
	4.001	24.9	7.007	25.0	10.002	25.0
	3.999	25.0	7.008	25.1	10.009	25.0
	3.997	25.1	7.009	25.0	9.994	25.0
	3.996	25.0	7.013	25.1	9.990	25.1
	4.002	25.0	7.013	24.9	9.992	25.0
Average	3.997		7.004		9.997	
SD	0.004		0.008		0.007	

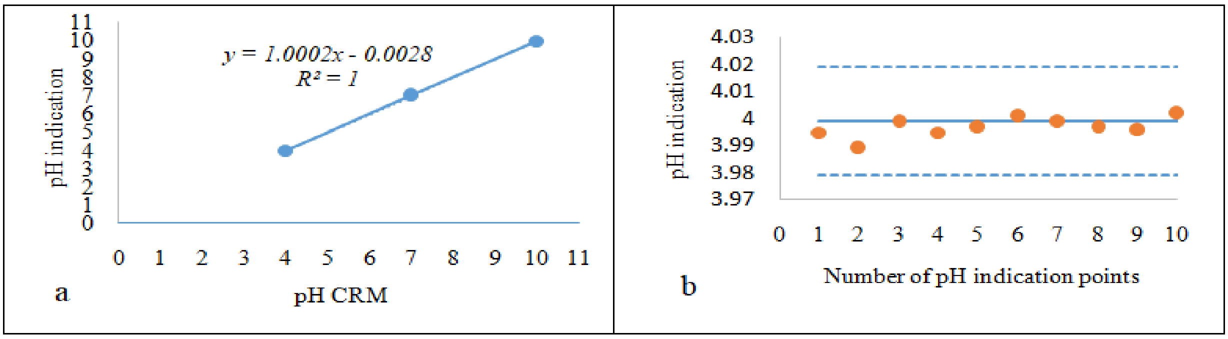

Figure 1: The calibration line (a) and the calibration indications of pH 3.999 within the uncertainty limits (b)

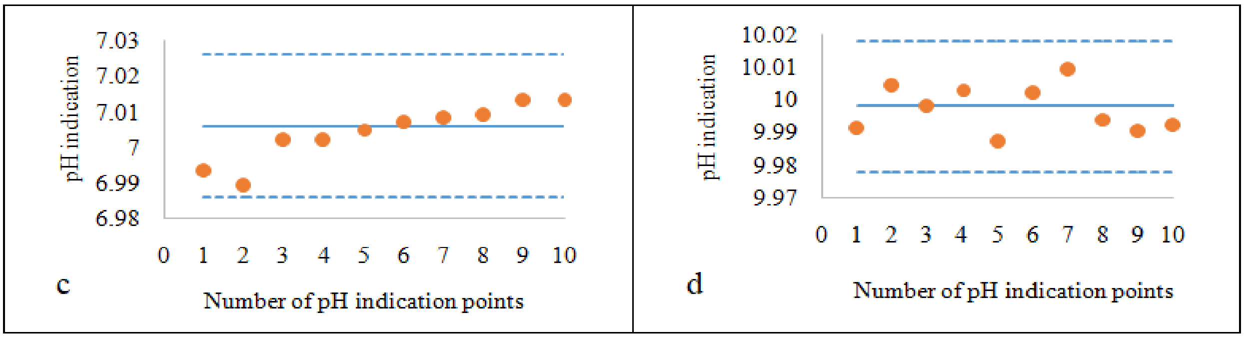

Figure 2: The calibration indications within the uncertainty limits of pH 7.006 c and pH 9.998 (d).

3.1. Uncertainty of measurements

3.1.1. Specifying the measurand

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The uncertainty estimation of the multipoint calibration of pH-meter was carried out using the bottom-up approach based on ISO GUM and EURACHEM/CITAC Guide CG4 [7,19]. The specified measurand is the *pH(x)* and the mathematical model of this measurement is expressed in equation 1.

$$pH(x) = a\,pH(s) + b \qquad (1)$$

where

pH(x) : measured pH
a : slope of the calibration line
pH(s) : pH of the CRM
b : intercept of the calibration line

From this model, the explicit sources of uncertainty that can be identified are: pH of the CRM, slope (*a*) and intercept (*b*) of the calibration line. Other implicit sources of uncertainty are the effect of temperature on the slope of the electrode system, resolution and drift of the pH-meter in addition to the repeatability of pH measurements as it can be seen in the fishbone diagram in Figure 3.

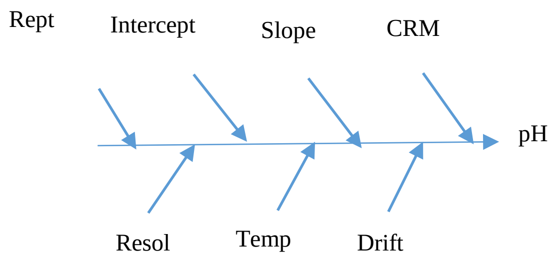

Figure 3: Fishbone showing the uncertainty sources

Because of the need to estimate the contribution of the implicit sources of uncertainty, the model should be modified to accommodate these sources. Since the temperature is measured in °*C* we have introduced the term $\partial\Delta t$, while for the resolution, drift and repeatability which are all expressed in pH units, we introduced the term ∂pH_{xn}. Thus the mathematical model was modified as shown in equation 2. This modification has been carried out in such a way that ∂pH_{xn} equals zero so that its introduction does not influence the value of *pH(x)*. However, uncertainty of this term influences the standard uncertainty $u(pH_x)$ associated with the value of pH(x). It has been reported that $u\,\partial pH_{xn}$ is the standard uncertainty originating directly from the operation of pH measurements and is defined as in equation 3 [16].

$$pH(x) = a\,pH(s) + b + \delta\Delta t + \delta pH_{xn} \qquad (2)$$

$$u(\partial pH_{xn}) = \sqrt{u(\partial pH_{xn}, resol)^2 + u(\partial pH_{xn}, drift)^2 + u(\partial pH_{xn}, rept)^2} \qquad (3)$$

In order to calculate this uncertainty term, the resolution of pH-meter (0.001) was divided by 2, and since no information is given about this uncertainty, a rectangular distribution was assumed and uncertainty was divided by √3 to give a contribution of 0.0003 according to equation 4 [6].

$$u_{Resol} = \frac{Resolution}{2\sqrt{3}} \qquad (4)$$

For uncertainty of the pH-meter drift, a figure of 0.01 pH unit was assumed because there was no available history about the drift. Assuming a rectangular distribution, this 0.01 was divided by √3 to obtain the standard uncertainty as 0.0058 according to equation 5.

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$$u_{Drift} = \frac{Drift}{\sqrt{3}} \qquad (5)$$

Uncertainty of the repeatability of measurements was calculated at each calibration point by dividing the standard deviation, *SD* of the mean of 10 pH indications by $\sqrt{n}$ ($n=10$) using equation 6. The obtained results were found 0.004 for pH 3.999, 0.008 for pH 7.006 and 0.007 for pH 9.998.

$$u_{\mathrm{Re}\,pt} = \frac{SD}{\sqrt{n}} \qquad (6)$$

The combined uncertainty contributions of u_{Resol}, u_{Drift} and u_{Rept} at each calibration point have been calculated as follows [19]:

$$u_{pHxn,3.999} = \sqrt{(0.003)^2 + (0.0058)^2 + (0.004)^2} = \pm 0.008$$

$$u_{pHxn,7.006} = \sqrt{(0.003)^2 + (0.0058)^2 + (0.008)^2} = \pm 0.01$$

$$u_{pHxn,9.998} = \sqrt{(0.003)^2 + (0.0058)^2 + (0.007)^2} = \pm 0.01$$

3.1.2. Uncertainty of the pH CRM

From the certificate of each pH CRM, the expanded uncertainty was reported as ±0.02 pH at confidence level 95%. Therefore, it was divided by 2 to calculate the standard uncertainty as ±0.01 in case of each pH CRM [6].

3.1.3. Uncertainty of the slope, *u(a)*

The calibration function $y = 1.0002\,x - 0.0028$ was obtained from the calibration line shown in Figure 1(a) above, where 1.0002 is the slope and -0.0028 is the intercept. The standard deviation of regression, *S*, was calculated using equation 7 indicated in ISO Guide 35 and was found 0.0066 [22].

$$S = \sqrt{\frac{\sum_{i=1}^{N}(y_i - b - a\,x_i)^2}{N-2}} \qquad (7)$$

where

N : is the number of measurements in the calibration process

y_i : is the pH indication

b : is the intercept

a : is the slope

x_i : is the pH of CRM

The obtained value of S was used to calculate uncertainty of the slope, *u(a)* according to equation 8 shown in ISO Guide 35 [22].

$$u(a) = \sqrt{\frac{S^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}} \qquad (8)$$

where,

S : standard deviation of regression

x_i : is the pH CRM

$\bar{x}$: is the average pH of CRMs

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3.1.4. Uncertainty of the intercept, u(b)

Uncertainty of the intercept was calculated using equation 9 laid down in ISO Guide 35, in which *n* is the number of calibration points [22]. The obtained values of the slope and intercept were found 0.0016 and 0.0012 respectively.

$$u(b) = \sqrt{\frac{S^2 \sum_{i=1}^{n} x^2}{n \sum_{i=1}^{n} (x_i - \bar{x})^2}} \qquad (9)$$

3.1.5. Uncertainty due to the effect of temperature

The uncertainty reported in the calibration certificate of the temperature sensor installed in the pH-meter was multiplied by the sensitivity coefficient, $\Delta pH/\Delta t$ which was calculated by measuring the pH at 20 °C and at 25 °C then dividing the difference (y_1-y_2) by the difference in temperature, (x_1-x_2) according to equation 10.

$$\frac{\partial y}{\partial x} = \frac{y_1 - y_2}{x_1 - x_2} \qquad (10)$$

where

y_1 : *pH at 25 °C*

y_2 : *pH at 20 °C*

x_1 : *25 °C*

x_2 : *20 °C*

3.1.6 The sensitivity coefficients, c_i

The sensitivity coefficients were obtained by differentiation of the measurement model shown in equation 2 as follows:

$\delta pH_{(x)}/\delta pH_{(s)} = a$

$\delta pH_{(x)}/\delta a = pH_{(s)}$

$\delta pH_{(x)}/\delta b = 1$

$\delta pH_{(x)}/\delta pH_{xn} = 1$

3.1.7. The combined standard uncertainty

The combined standard uncertainty, u_c was calculated according to ISO GUM using equation 11 in which each sensitivity coefficient was multiplied by the uncertainty contribution and squared. The results obtained are shown in Table 2.

$$u_C = \sqrt{\left(\frac{\partial pH(x)}{\partial pH(s)} . u_{CRM}\right)^2 + \left(\frac{\partial pH(x)}{\partial a} . u_a\right)^2 + \left(\frac{\partial pH(x)}{\partial b} . u_b\right)^2 + \left(\frac{\partial pH(x)}{\partial \Delta t} . u_{\Delta t}\right)^2 + \left(\frac{\partial pH(x)}{\partial pHnx} . u_{pH_{nx}}\right)^2} \qquad (11)$$

The expanded uncertainty was calculated based on the standard uncertainties multiplied by a coverage factor *k=2* to provide a confidence level of approximately 95% using equation 12 and the results are given in Table 2.

$$U_{\exp} = u_c \; x \; k \qquad (12)$$

Table 2: The combined standard and expanded uncertainty of the multipoint calibration of pH-meter

pH	The combined standard uncertainty $u(x_i)$	The expanded uncertainty, U_{exp}
pH 4	0.018	0.035
pH 7	0.020	0.040
pH 10	0.023	0.045

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V. CONCLUSION

A procedure for estimation of the uncertainty of multipoint calibration of pH-meters with glass electrodes in the pH-mode based on ISO GUM has been developed. The identified sources of uncertainty were CRM pH, slope, and intercept, effect of temperature, repeatability, resolution and drift of the measuring system. The method was found capable to produce appropriate pH expanded uncertainties of ±0.035, ±0.040 and ±0.045 associated with pH of 3.997, 7.004 and 9.998 respectively. This uncertainty calculation procedure is very useful for the analytical laboratories measuring pH in the pH-mode.

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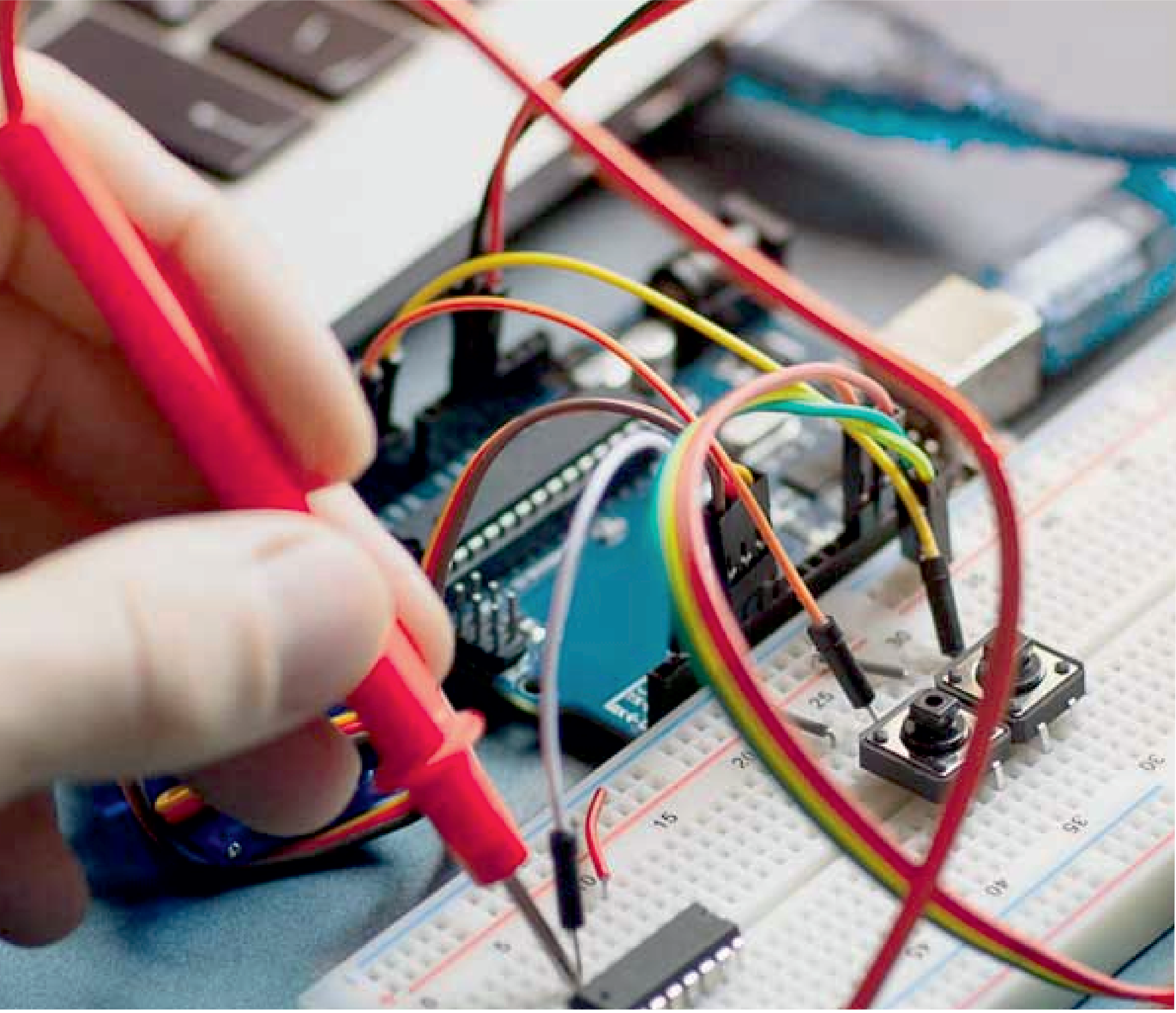

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