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Linearity of Microbalances Used for Gravimetric Method Calibration of Piston Pipettes, Determined by the Method of Small Mass Increments

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Measuring nonlinearity (linearity error) in high-resolution electronic balances, including microbalances, is challenging. Today's electronic balances are usually characterized by a small linearity error (with tolerance limits for nonlinearity specified by manufacturers in the order of several elementary divisions), and all criteria for measuring nonlinearity must meet or even exceed this tolerance limit. Linearity is determined over the full range of the balance at several measurement points (usually at least five points). The use of balances in the calibration of piston pipettes requires the determination of the linearity error within a very small working range. The paper describes a new method for testing the linearity of electronic balances used for the calibration of piston pipettes using the gravimetric method with small, constant mass increments, which corresponds to the process of calibrating piston pipettes. Studies have shown that the method of determining linearity using small mass increments gives more accurate results — yielding smaller linearity errors in the measuring range corresponding to pipette calibration. When incorporating the linearity component of the balance in the measurement uncertainty model for calibrating piston pipettes, the new method allows for reducing the uncertainty of pipette calibration. This is important for laboratories that calibrate pipettes, as it enables improvement in the calibration and measurement capability parameter, and for users of piston pipettes who receive pipettes with more accurate calibration.

topics: linearity, microbalances, calibration, piston pipette systems

1. Introduction

Among the many mechatronic devices using electrodynamic measuring transducers, electronic scales hold the largest share, as they are used for mass measurements with the highest accuracy. The advancements in the design and construction of such transducers, which we are currently witnessing, are a result of market expectations, and the designers of electronic scales have succeeded in building the most accurate weighing devices in the world in terms of elementary division [1]. One of the most popular and widely used laboratory groups of electronic scales are analytical scales and microbalances, which, in addition to standard laboratory weighing, are also used for tasks such as calibrating piston pipettes using the gravimetric method [2]. The most accurate electronic scales are based on the restoration of electromagnetic force, also known as electromagnetic force compensation. These weighing sensors consist of a parallel guiding mechanism, which ensures accurate placement of the weighed object, one or more levers, and an electromagnetic system (magnet and coil) that functions as the counterweight in a two-pan scale. The traditional triangular edges of the scale knife are replaced with flexible bearings. By altering the lever ratio, balancing forces smaller than 1 N with much larger ones is possible. Nowadays, systems with one, two, or even three levers are common, depending on the load range. The balance must maintain its parallelogram shape to ensure equilibrium, regardless of where the load is placed on the pan [3]. One of the significant challenges associated with electronic balances is maintaining an appropriate level of nonlinearity, which necessitates performing a linearity parameter test, usually during calibration. The issue of testing the linearity of electronic balances is not sufficiently covered in the literature. Still, the authors of [4] suggested that the most intuitive and straightforward methods of measuring nonlinearity are likely the absolute method or the difference method. In these methods, if the linearity test range is mL and needs to be tested at $n+1$ points, n precisely known mass standards $m_0 = mL/n$ must be used.

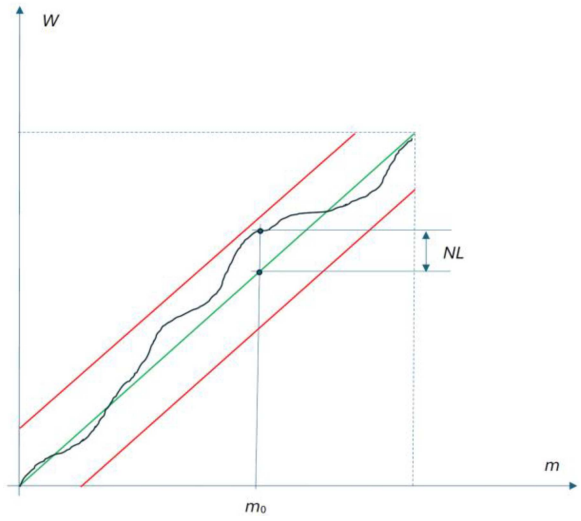

Fig. 1. Linearity deviation (exaggerated) between load m and weighing value W. A possible deviation of the sensitivity (slope of the straight line) does not count as linearity deviation. The green line is the linear characteristic curve of a weighing instrument between load m and weighing value W.

Alternatively, a set of n weights of increasing masses, specifically $m_0, 2m_0, \ldots, n\,m_0$, can be used. In this case, successive weights should replace the previous ones on the scale. However, the mass of each weight must be known precisely. First, a reading is taken without any load. Then the first weight is placed on the pan and read. The next weight is added and read, and so on until all the weights are placed on the pan and the measurements are recorded. This results in $n + 1$ positions and readings, i.e., measuring points. These methods are used to test linearity over the entire measuring range. Linearity error is one of the systematic components in the classical analysis of errors in electronic weighing devices. In the terminology of the International Vocabulary of Metrology (VIM), the concept of linearity error (nonlinearity) is not described. The definition of linearity for non-automatic scales (mechanical and electronic) can be found in the "Dictionary of Weighing Terms — A Guide to the Terminology of Weighing" (Springer, 2009). This definition describes linearity as the ability of a weighing instrument to follow the linear relationship (Fig. 1) between a load m and the indicated weighing value W.

We can compare this definition with nonlinearity, which tells us that nonlinearity is equal to 1. Deviation of the characteristic curve from the straight line between zero load and nominal load that is defined by the sensitivity. By definition, the linearity deviation of the starting and finishing point of this straight line is zero, and a possible deviation of the sensitivity (slope of the straight line) does not count as linearity deviation [g].

High-precision electronic non-automatic scales have a very wide range of applications, they can be found in the areas of pharmaceuticals, biotechnology, and food, and in various research laboratories. Non-automatic scales have several parameters characterizing their metrological properties. These include error of indication, error of indication with a working taring (zeroing) device, error of indication resulting from an eccentric load, repeatability (precision), excitability, and sensitivity. The previously mentioned linearity error is a parameter that can be very important in some applications of electronic non-automatic scales. One such solution is the use of a non-automatic electronic scale to perform calibration procedures for single-channel pipettes using the gravimetric method. The normative requirements for piston pipettes are specified in the ISO 8655 series of standards for piston-operated volume measuring instruments. Part 6 of the ISO 8655-6 standard describes the reference gravimetric measurement procedure used to determine and verify the volume of piston pipettes. This method can be used as part of the supervision of measuring equipment. It should be noted here that the need to supervise measuring equipment, such as a piston pipette, results from the requirements of the ISO 17025:2018-02 standard "General requirements for the competence of testing and calibration laboratories — point 6.4 Equipment" and from the requirements of the PN-EN ISO 9001:2015-10 standard "Quality management systems — point 7.1.5.2 Measurement traceability". Regardless of the normative requirements within the so-called life cycle of a measuring instrument, it should be periodically checked and its accuracy verified while maintaining measurement traceability. For testing electronic scales, appropriate mass standards with a calibration certificate are necessary. It is worth noting here the dissemination process in terms of consistency of mass measurements after the redefinition of the SI unit system [5]. The assessment of the pipette's performance mainly concerns its metrological properties, such as the correctness and precision of measurements. In the process of calibrating piston pipettes using the gravimetric method, the mass of the liquid discharged is recorded. Therefore, the weighing results should be converted to volume. For this purpose, we choose a method whose mathematical model is presented in Sect. 2.1, namely calibration of piston pipettes using the gravimetric method. It involves measuring the mass of the discharged volume of liquid. Microbalances are most often used to calibrate piston pipettes in the range of 1–10 μl. The basic method involves measuring the mass of an empty vessel and then measuring the mass with the liquid poured out through the pipette. Due to the difficulty of measurement and the effect of evaporation during measurement, this method is increasingly being replaced by the use of a vapor curtain, and measurement of the liquid discharged into one vessel using the tare/zeroing function of

Fig. 2. Mass standards made of mother-of-pearl.

Fig. 3. Research object — electronic ultramicrobalance Mettler Toledo XPR6U.

the scale. The measurement takes place in a much shorter time when using a "vapor curtain", which allows for minimizing the effect of evaporation [6].

2. Materials and methods

2.1. Mass standards for linearity testing

To determine the linearity error, standard mass standards and a set of ten special mass standards of ≈ 10 mg were prepared. The test was performed using standard mass standards made of stainless steel by the requirements of the OIML R 111 document, and using standards made of "mother-of-pearl" in the shape of a "pearl" (Fig 2). Each standard was calibrated and identified by its shape (steel standards) and by its appropriate color ("mother-of-pearl" standards).

Steel standards have an appropriate calibration certificate. The "mother-of-pearl" standards are calibrated using the ABBA method for three measurement cycles described in the OIML R 111 document. The process consists of determining the mass by using the reference measurement standard A and the tested/calibrated standard B. The average difference r_i for the ABBA method for each calibrated working standard was determined using

$$r_i = \bar{B} - \bar{A}, \tag{1}$$

where r_i is the difference in means $B-A$ of the i-th measurement, $\bar{B}$ is the average reading for the tested/calibrated standards B the given i-th ABBA series, and $\bar{A}$ is the average reading for the reference measurement standard A for the given i-th ABBA series.

The mean value of the differences r_i was calculated according to

$$\bar{r} = \frac{1}{n}\sum_{i=1}^{n} r_i, \tag{2}$$

where n is a number of ABBA series measurements.

2.2. Research object

The first tests were performed on an ultra-microanalytical non-automatic electronic balance manufactured by Mettler Toledo with a scale interval of $d = 0.1$ μg and a maximum load of max 6.1 g (see Fig. 3). The test object is used for high-accuracy mass measurements. The tests were performed at the Mass Laboratory of the Central Office of Measures in Warsaw (Poland), where the environmental conditions required for the calibration of the highest accuracy mass standards are maintained in accordance with the OIML R-111 Table C1 document (for E1 standards).

2.3. Research method

For the tested object, linearity parameters were determined using two methods for two different measurement ranges. The first measurement range included 10 measurement points spaced apart by a value close to the average value of special working measurement standards. This state reflects the implementation of the liquid weighing method during the calibration of piston pipettes. The first method consisted of determining the linearity parameter for ten steps with increasing load. After zeroing the balance, the first (white) special working measurement standard was placed on the weighing pan, and after the result stabilized, the reading was recorded. Then, the next (pink) working measurement standard was placed on the weighing pan, and after the result stabilized, the reading was recorded. The operation was repeated in subsequent steps for the remaining eight working measurement standards of appropriate colors: yellow, orange, purple, green, glossy green, blue, light blue, and glossy blue. The second method consisted of determining the linearity parameter (similarly to the first method) for ten steps with increasing load using the tare/zeroing device available in non-automatic electronic scales —

TABLE I

Linearity error using the basic method.

No.	Standards value [g]	Indication of balance [g]	Linearity error E_{LinP} [g]
1	0.0139801	0.0139803	0.0000002
2	0.0308033	0.0308044	0.0000010
3	0.0447658	0.0447691	0.0000033
4	0.0601431	0.0601453	0.0000022
5	0.0737895	0.0737932	0.0000037
6	0.0875918	0.0875970	0.0000052
7	0.1025042	0.1025096	0.0000054
8	0.1192169	0.1192243	0.0000074
9	0.1334053	0.1334146	0.0000093
10	0.1471647	0.1471773	0.0000126

TABLE II

Linearity error using taring/zeroing device.

No.	Standards value [g]	Indication of balance [g]	Linearity error E_{LinP} [g]
1	0.0139801	0.0139802	0.0000001
2	0.0168232	0.0168231	−0.0000001
3	0.0139625	0.0139632	0.0000007
4	0.0153773	0.0153776	0.0000003
5	0.0136464	0.0136471	0.0000007
6	0.0138023	0.0138032	0.0000009
7	0.0149124	0.0149133	0.0000009
8	0.0167127	0.0167144	0.0000017
9	0.0141884	0.0141899	0.0000015
10	0.0137594	0.0137616	0.0000022

the tare/zeroing devices are commonly used when calibrating piston pipettes using the gravimetric method. After zeroing the balance, the first special working measuring standard (white) was placed on the weighing pan, and after the result stabilized, the reading was recorded and the tare/zeroing device was used. After taking/zeroing the balance, another working measuring standard (pink) was placed on the weighing pan, after the result stabilized, the reading was recorded and the tare/zeroing device was used. The operation was repeated in the following steps for the remaining eight working measuring standards of appropriate colors: yellow, orange, purple, green, glossy green, blue, light blue, and glossy blue. The linearity parameter was determined from the equation

$$\mathrm{E_{Lin}} = I_W - m_{\mathrm{ref}}, \tag{3}$$

where Lin is linearity (linearity error), I_W — indication of weighing instrument, m_{ref} — mass standard value determined during calibration.

2.4. Research results

In this section, the measurement results are presented. Table I shows the results of E_{LinP} linearity tests using the basic method of increasing load for ten similar loads. Table II shows the results of E_{LinT} linearity tests at the same measurement points using a taring/zeroing device after each measurement. The results represent the average value of the measurements taken during the tests.

Table III presents the results of the difference in E_{Lin} linearity errors calculated according to

$$E_{\mathrm{Lin}} = E_{\mathrm{LinP}} - E_{\mathrm{LinT}}. \tag{4}$$

Figure 4 graphically shows the difference in the linearity error values determined by the basic method when using small mass increments (Series 1) and by the small mass increment method when using a taring/zeroing device (Series 2).

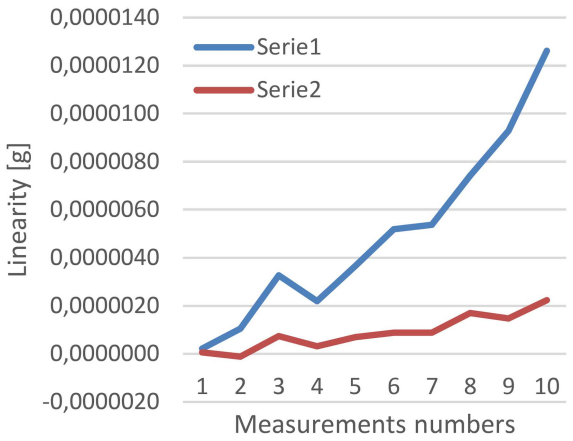

Fig. 4. Measurement results in graphical form given by Series 1 (E_{LinP}) and Series 2 (E_{LinT}).

TABLE III

Difference between $E_{LinP}$and E_{LinT}.

No.	Linearity E_{LinP} [g]	Linearity E_{LinT} [g]	Linearity E_{Lin} [g]
1	0.0000002	0.0000001	0.0000002
2	0.0000010	−0.0000001	0.0000012
3	0.0000033	0.0000007	0.0000025
4	0.0000022	0.0000003	0.0000019
5	0.0000037	0.0000007	0.0000030
6	0.0000052	0.0000009	0.0000043
7	0.0000054	0.0000009	0.0000045
8	0.0000074	0.0000017	0.0000057
9	0.0000093	0.0000015	0.0000078
10	0.0000126	0.0000022	0.0000104

3. Conclusions

The authors consider the proposed method of testing the linearity of electronic non-automatic scales using the small mass increment method as an important step allowing for a new, more accurate approach to testing this parameter. This is particularly important when the linearity parameter of scales is included in the uncertainty budgets for scale calibration, as well as in budgets that include this parameter such as for calibration of piston pipettes. First of all, this method may concern determination of linearity parameter for scales used for calibration of piston pipettes using an evaporation trap and a tare/zeroing function. In this case, the method of testing linearity parameter using ten almost identical (in terms of value) material mass standards reflects the process of pouring the same volume of liquid into a weighing vessel ten times. The linearity parameter (linearity error as a systematic component of error) determined in this way allows for the use of an appropriately accurate correction to compensate for the error in the indication of the liquid mass measurement. This method can be improved and adapted to various tested pipette volumes. The continuous development of devices from the "liquid handling" category, which include piston pipettes, has led to the development of the method towards the use of mass standards smaller than 1 mg, which are presented in the publications indicated in the literature [7–9]. In the next step, the authors plan to perform tests for other balances with lower accuracy and attempt to extend the tested method with 1 mg standards and to produce standards below 1 mg. An example of the use of standards below 1 mg has already been presented in [1] in the application to the study of an ultra-accurate mass comparator with an elementary scale of 10 ng. The authors also hope that after conducting additional, planned tests, it will be possible to propose the use of this method to test the linearity of balances not only for the calibration of piston pipettes. In the next planned studies, micro-mass standards made of other materials will also be used.

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