

Validation of Metrohm burets

Of interest to:

General analytical laboratories

A B F I L 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16

Summary

Among other things, **GLP (Good Laboratory Practice)** requires that the accuracy and precision of analytical instruments are checked at regular intervals using **Standard Operating Procedures (SOPs)**.

Metrohm recommends the use of the gravimetric test method described below as the Standard Operating Procedure for validating Dosing and Exchange Units.

This gravimetric linearity test can be used for the following purposes:

- Quality assurance by the manufacturer
- Quality assurance of analytical or other measuring systems by the user

The described method is not an official reference method. The metrological requirements placed on piston burets, in particular the maximum permissible measurement errors, are specified in the ISO Standards 8655-1 to 8655-6.

Instruments and accessories

- Metrohm dosing device with the Dosing or Exchange Unit to be checked
- Weighing vessel with sufficient capacity for a complete measurement series
The loss of water by evaporation should be kept as low as possible during the whole test procedure. The weighing vessel height-to-diameter ratio should be at least 3 : 1.
- Thermometer with a standard measurement uncertainty of max. 0.2 °C
- Barometer with a standard measurement uncertainty of max. 0.5 kPa
- Analytical balance according to OIML R 76-1

The minimum requirements placed on the balance with regard to the Dosing or Exchange Unit that is to be checked with it are as follows:

Cylinder volume of the Dosing or Exchange Unit	Resolution of the display	Repeatability and linearity
1...10 mL	0.1 mg	±0.2 mg
20...50 mL	1 mg	±2 mg

Test conditions

Test liquid

If possible, degassed distilled or deionized water («Quality 3» water according to ISO 3696) whose temperature is in equilibrium with the surroundings should be used.

Dismantling and assembly of the buret unit

Before the test the buret unit should be dismantled, cleaned and then reassembled. Please consult the corresponding Instructions for use. (See ISO 8655-6, Chapter 6.1: Before the test any instruments that in proper use have to be dismantled and reassembled (e.g. for cleaning purposes) must be dismantled and reassembled at least once according to the instructions manual provided by the manufacturer.)

Test room

The test room should be free from drafts and guarantee stable ambient test conditions. The relative humidity should be above 50% and the room temperature should be constant (± 0.5 °C) between 15 and 35 °C. Prior to the test, the instruments and the test liquid must be allowed to stand in the test room for a sufficient length of time (approx. 2 h as a rule of thumb) to achieve equilibrium with the ambient room conditions.

Test cycle duration

The test cycle duration (one single dosing and the subsequent weighing) should ideally not exceed 60 s in order to avoid weighing errors resulting from evaporation of the test liquid. The duration of the individual test cycles should be as uniform as possible.

Test procedure

Preparation

The tests must be carried out in a draft-free room under constant ambient conditions.

The Dosing or Exchange Unit to be checked is filled bubble-free with the test liquid and placed as close as possible to the balance. The test setup must not be exposed to direct sunlight, vibrations or drafts.

The buret tip is firmly attached to a support rod. During the dosing procedure it must not be moved or touched. If possible, the buret tip should be led directly into the balance weighing chamber from above (cover the weighing chamber; see Appendix 1).

The clean weighing vessel base is covered to a height of 1...2 mm with the test liquid. The vessel containing the water is placed in the balance weighing chamber, which is then closed.

The following dosing rates and Eppendorf tips should be used for carrying out the tests at different cylinder volumes (see also Appendix 1):

Nominal cylinder volume	Eppendorf tip to be used; dosing rate
50 mL	1000 µL (blue); 100 mL/min
20 mL	1000 µL (blue); max. mL/min
10 mL	200 µL (yellow); max. mL/min
5 mL	200 µL (yellow); max. mL/min
2 mL	200 µL (yellow); max. mL/min
1 mL	200 µL (yellow); max. mL/min; special setup

It is important that a stream of liquid is produced during the dosing procedure. The size of the water droplets retained on the tip must be constant; although a just fallen drop is to be preferred (alternative: an unchanging drop of the same size after each dosing step).

Prior to each measurement series, the Dosing or Exchange Unit must be subjected to a preparation step (PREP). In addition, one or two preliminary dosing steps with approx. 20% of the cylinder volume should be carried out using the corresponding dosing or filling rate; this guarantees a uniform droplet size even for the first measured dosing step.

In order to keep evaporation of the test liquid as small as possible, an additional vessel containing water and an immersed filter paper (to increase the surface area) can be placed in the weighing chamber.

Test cycle

The Dosing or Exchange Unit should first be cleaned and serviced according to the Instructions for use (at the latest when the test specifications are no longer achieved), as resinified grease may lead to inaccurate dosing.

The following parameters must be determined and recorded:

- Temperature t of the water and the ambient air in °C
- Current absolute atmospheric pressure p_A in mbar (not corrected to sea level!)

First the weight of the weighing vessel with the pre-dispensed test liquid must be determined. This value represents the tare weight.

Within a test cycle the buret then dispenses the test liquid into the weighing vessel until the selected volume has been reached. Afterwards the weighing vessel is weighed and the mass of the added liquid calculated.

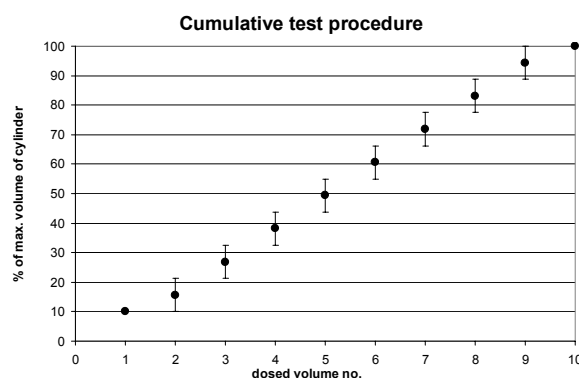
For the Metrohm linearity test the ten volumes to be dispensed must be selected in the following way:

- The smallest test volume is exactly 10%, the largest one exactly 100% of the cylinder volume of the buret unit used.
- The additional eight test volumes should be evenly distributed across the given volume range, but be selected in a random way.

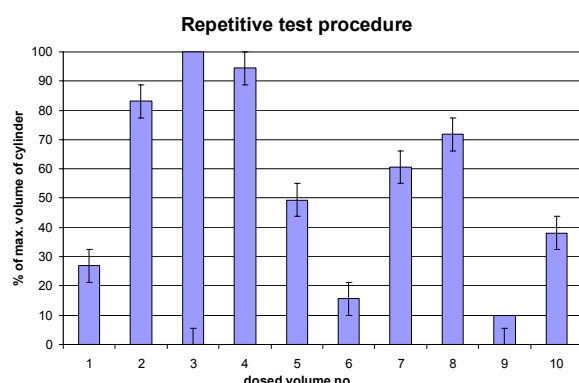
This procedure ensures that the whole volume range of the dosing cylinder is covered, which allows the linearity of the dispensed volumes to be reliably checked.

Different procedures can be used for carrying out the measurement series:

In a **cumulative** procedure the test volumes are dispensed from one cylinder filling without any refilling. This is the quickest method:



In a **repetitive** procedure one test volume is dispensed and the cylinder then refilled. Each dosing thus starts with a cylinder that is completely full:



Weighing does not take place until the respective test volume has been completely dispensed into the weighing vessel. The test liquid must be dispensed through an additionally attached pipet tip, which ensures that the flow stops abruptly and no droplets can be formed.

Calculations

Calculating the actually dispensed volume

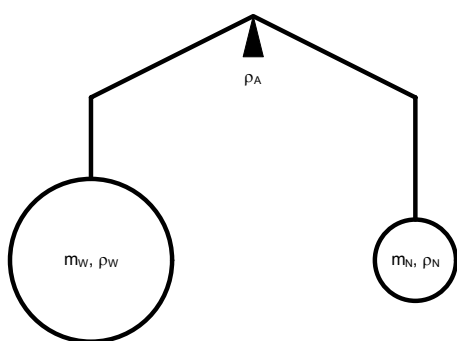
Conventional weight value and true mass

Definition [1]:

«The conventional weight value of a body is equal to the mass of a standard reference mass with a density of 8000 kg m^{-3} , which keeps this body at equilibrium at a temperature of $20 \text{ }^\circ\text{C}$ and a density of air of 1.2 kg m^{-3} .»

From this definition it can be seen that for bodies with a density of 8000 kg m^{-3} the conventional weight value and the mass are the same.

Calculating the true mass m_W from the conventional weight value m_N



m_W = mass of the object (water) in kg

m_N = mass of the standard reference mass in kg

ρ_W = density of the object (water) in kg m^{-3}

ρ_N = density of the standard reference mass in kg m^{-3}

ρ_A = density of the air in kg m^{-3}

g = gravitational acceleration in m s^{-2}

The forces are in a state of equilibrium when the weight force of the object minus the buoyancy acting on the object is the same as the weight force of the standard reference mass minus the buoyancy acting on the standard reference mass:

$$(m_W \cdot g) - \left(\frac{m_W \cdot \rho_A \cdot g}{\rho_W} \right) = (m_N \cdot g) - \left(\frac{m_N \cdot \rho_A \cdot g}{\rho_N} \right) \quad (1)$$

$$m_W \cdot \left(1 - \frac{\rho_A}{\rho_W} \right) = m_N \cdot \left(1 - \frac{\rho_A}{\rho_N} \right) \quad (2)$$

$$m_W = \frac{m_N \cdot \left(1 - \frac{\rho_A}{\rho_N} \right)}{\left(1 - \frac{\rho_A}{\rho_W} \right)} \quad (3)$$

Calculating the dispensed water volume V_W

When calculating the dispensed water volume V_W from its conventional weight value m_N the following conversion factor f is obtained (The value shown on the balance corresponds to the weight value of a body with the same density as the standard reference mass. For this reason the conventional weight value corresponds to the value m_N and not m_W):

$$V_W = \frac{m_W}{\rho_W} = f \cdot m_N \quad (4)$$

$$f = \frac{m_W}{\rho_W \cdot m_N} \quad (5)$$

V_W = actually dispensed water volume in m^3

f = conversion factor in $\text{m}^3 \text{ kg}^{-1}$

By inserting (3) in (5) the following equation is obtained for the factor f :

$$f = \frac{\left(1 - \frac{\rho_A}{\rho_N} \right)}{\rho_W \cdot \left(1 - \frac{\rho_A}{\rho_W} \right)} = \frac{1}{\rho_N} \cdot \left(\frac{\rho_N - \rho_A}{\rho_W - \rho_A} \right) \quad (6)$$

As the water volume V_W corresponds to the product of the conversion factor f and the weight value m_N (see equation (4)), it then follows:

$$V_W = m_N \cdot f = \frac{m_N}{\rho_N} \cdot \left(\frac{\rho_N - \rho_A}{\rho_W - \rho_A} \right) \quad (7)$$

Calculating the density ρ_W of the water [2]

The density of air-free water between $0 \text{ }^\circ\text{C}$ and $40 \text{ }^\circ\text{C}$ can be calculated as follows:

$$\rho_W = \sum_{n=0}^5 c_n \cdot t^n \quad (8)$$

$$\rho_W = c_0 + (c_1 \cdot t) + (c_2 \cdot t^2) + (c_3 \cdot t^3) + (c_4 \cdot t^4) + (c_5 \cdot t^5) \quad (9)$$

ρ_W = density of the water in kg m^{-3}

c_0 = $9.99839564 \cdot 10^2 \text{ kg m}^{-3}$

c_1 = $6.7998613 \cdot 10^{-2} \text{ kg m}^{-3} \text{ }^\circ\text{C}^{-1}$

c_2 = $-9.1101468 \cdot 10^{-3} \text{ kg m}^{-3} \text{ }^\circ\text{C}^{-2}$

c_3 = $1.0058299 \cdot 10^{-4} \text{ kg m}^{-3} \text{ }^\circ\text{C}^{-3}$

c_4 = $-1.1275659 \cdot 10^{-6} \text{ kg m}^{-3} \text{ }^\circ\text{C}^{-4}$

c_5 = $6.5985371 \cdot 10^{-9} \text{ kg m}^{-3} \text{ }^\circ\text{C}^{-5}$

t = water temperature in $^\circ\text{C}$

Calculating the density ρ_A of the air

The density of air can be calculated as follows:

$$\rho_A = \frac{k_1}{1 + k_2 \cdot t} \cdot \frac{p_A}{k_3} \cdot 1000 \quad (10)$$

ρ_A = density of the air in kg m^{-3}
 k_1 = 0.001293 kg m^{-3}
 k_2 = 0.00367 $^{\circ}\text{C}^{-1}$
 k_3 = 1013 mbar
 p_A = air pressure in mbar
 t = air temperature in $^{\circ}\text{C}$

Calculating the mean of the dispensed volumes

After a complete series of 10 measurements (10 test volumes) the slope of the linear regression (actually dispensed water volume V_{act} as a function of the theoretical water volume V_{theo}) is calculated. Under the assumption $V_{n+1} = 0.000$ mL as an additional value the equations given below apply. (As a result of this assumption the value pair 0/0 is generated and automatically included in the calculation.)

The 10 dispensed water volumes V_W are added together and the total is divided by 11 in order to obtain the mean of the dispensed volumes at the test temperature. This value can be given in μL or mL:

$$\bar{V} = \frac{1}{n+1} \sum_{i=1}^{n+1} V_{W,i} \quad (11)$$

\bar{V} = arithmetic mean of n measurements of the quantity V_W
 $V_{W,i}$ = individual value for a measurement of the quantity V_W
 n = number of measurements of the quantity V_W (n measurements, but $n + 1$ values, see above)

Calculating the slope of the linear regression

$$\text{Slope} = \frac{\sum_{i=1}^{n+1} (V_{\text{theo},i} - \bar{V}_{\text{theo}}) \cdot (V_{\text{act},i} - \bar{V})}{\sum_{i=1}^{n+1} (V_{\text{theo},i} - \bar{V}_{\text{theo}})^2} \quad (12)$$

\bar{V} = arithmetic mean of n measurements of the quantity V_{act}
 V_{act} = individual measured value for the corresponding V_{theo}
 V_{theo} = theoretical measured value (selected test volume)
 \bar{V}_{theo} = arithmetic mean of the $n + 1$ theoretical measured values V_{theo} (\rightarrow calculated according to equation (11))

Calculating the dosing error \rightarrow systematic measurement error

According to ISO 8655 the absolute dosing error for the nominal cylinder volume is defined as follows:

$$e_{\text{abs}} = V_{\text{act}} - V_{\text{theo}} \quad (13)$$

e_{abs} = absolute dosing error = systematic measurement error

V_{act} = actually dispensed water volume

V_{theo} = theoretical water volume (test volume)

Error limits

Decision criteria for a dosing cylinder:

- Slope (linearity) of the dispensed volumes
- Absolute or relative systematic error for the nominal cylinder volume

If a decision criterion is infringed then the Dosing or Exchange Unit has not passed the test. \rightarrow Failed the test!

Slope:

The slope must lie within the range 1.000 ± 0.003 .

Absolute or relative systematic error for the nominal cylinder volume:

Nominal cylinder volume mL	Absolute or relative systematic error for the nominal volume	
	$\pm\mu\text{L}$	$\pm\%$
1	6	0.6
2	10	0.5
5	15	0.3
10	20	0.2
20	40	0.2
50	100	0.2

The values given in the table must not be exceeded.

Please note that – according to ISO 8655 – the limit value for the relative systematic error is only defined for the nominal cylinder volume. This means that the relative error can only be used as a decision criterion for this test volume, but not for smaller volumes. For part-volumes only the absolute error, which is valid for the whole volume range of the dosing cylinder, can be used as a hard criterion.

Practical information on dosing in general

- If in an analysis the same Dosing or Exchange Unit is used for the titer determination and for the titration of the samples then the absolute accuracy of the dispensed volume does not matter as any systematic error is already taken into account in the titer. It is only important that there is a linear relationship between the weight values read off at the balance and the respective theoretical volumes V_{theo} .
- The volumes dispensed with a Dosing or Exchange Unit should always be within the range between 10 and 100% of the nominal volume of the glass cylinder. Otherwise a different cylinder size should be used for dosing.
- The cylinder and piston should always be visually inspected before use: No crystals should have crystallized out in the cylinder; no film of liquid should be present between the piston and the connecting rod. → Otherwise a service must be carried out according to the Instructions for use.
- Dosing and Exchange Units should be cleaned and serviced at regular intervals (recommendation: every six months or more frequently). This helps to avoid problems and allows any inaccuracies to be discovered at an early stage.
- During servicing no individual parts should be replaced. We recommend that the piston and cylinder (including the base) are always replaced together. → Long working life of the parts.
- Complete replacement is preferable to repair. Do not remove the valve disk from the distributor piece. Do not remove the glass cylinder from the cylinder base. If possible always replace the whole unit!
- Always use a buret unit with glass cylinder for titration and precise measuring out of liquids (dosing, pipetting). Plastic cylinders are only intended for use with media that attack glass (alcoholic KOH, HF, etc.); they are less accurate.
- Please check at regular intervals that tubing and tubing connections are intact.
- We recommend to subject the Dosing or Exchange Unit to a preparation step (PREP) each day prior to use. This helps to save time and avoid problems.
- Solutions that tend to crystallize out (e.g. KF reagents) should be removed from the Dosing or Exchange Unit if it is to be stored for a long time (EMPTY).
- For all dosing processes the buret tip should be mounted at approximately the same height as the liquid surface in the storage vessel. → Hydrostatically communicating vessels during valve switching.
- After dosing, wait approx. 1...2 s before refilling the cylinder. This is particularly important for large cylinder volumes in order to achieve pressure compensation.

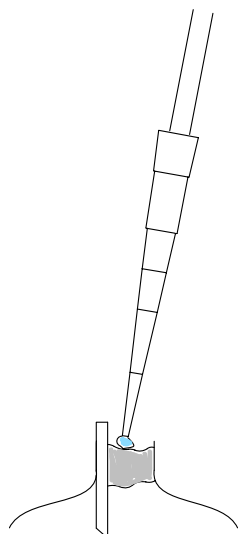
- When dispensing viscous liquids the dosing and filling rates should be reduced accordingly in order to prevent the formation of a vacuum within the system.

Literature

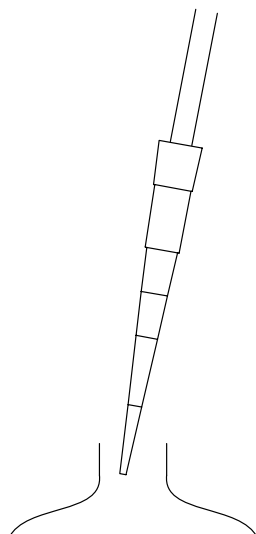
- [1] Nachr. Chem. Tech. Lab. 38 (1990) Nr. 3, p. M8
 - [2] H. Wagenbreth, W. Blanke, Die Dichte des Wassers im Internationalen Einheitensystem und in der Internationalen Praktischen Temperaturskala von 1968, PTB-Mitteilungen 81 (1971) 412–415
- ISO 3696:1987, Water for analytical laboratory use – Specification and test methods
 - ISO 8655-1:2002, Piston-operated volumetric apparatus – Part 1: Terminology, general requirements and user recommendations
 - ISO 8655-2:2002, Piston-operated volumetric apparatus – Part 2: Piston pipettes
 - ISO 8655-3:2002, Piston-operated volumetric apparatus – Part 3: Piston burettes
 - ISO 8655-4:2002, Piston-operated volumetric apparatus – Part 4: Dilutors
 - ISO 8655-5:2002, Piston-operated volumetric apparatus – Part 5: Dispensers
 - ISO 8655-6:2002, Piston-operated volumetric apparatus – Part 6: Gravimetric methods for the determination of measurement error
 - ISO/TR 20461:2000, Determination of uncertainty for volume measurements made using the gravimetric method
 - OIML R 76-1:1992, Nonautomatic weighing instruments – Part 1 : Metrological and technical requirements

Appendix

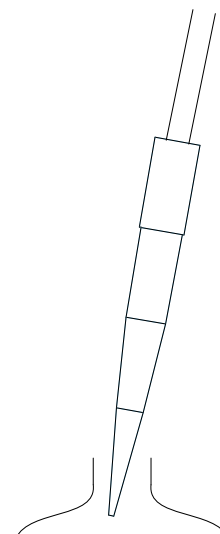
1. Test setup for carrying out the Metrohm linearity test



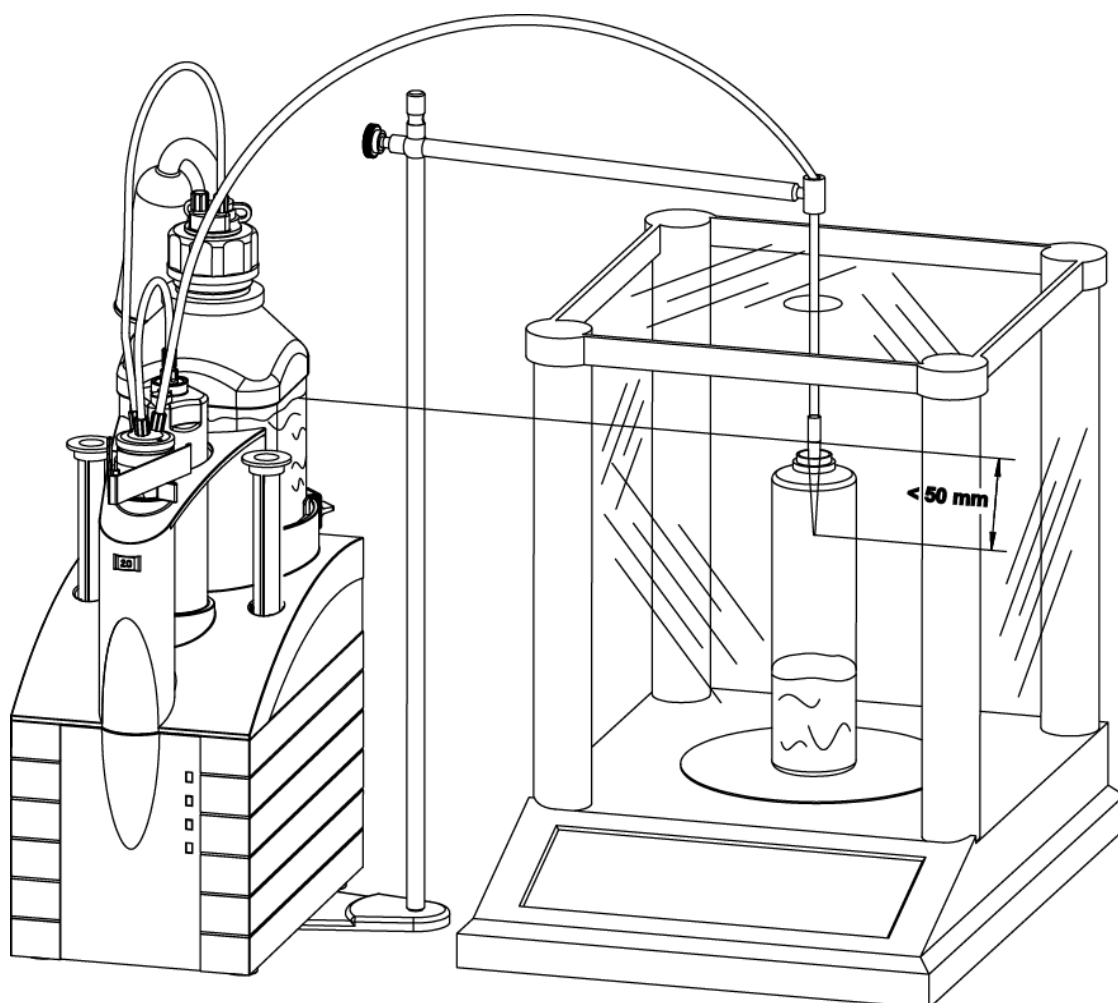
Cylinder volume 1 mL:
200 µL Eppendorf tip (yellow), dosing onto paper tissue



Cylinder volumes 2, 5 and 10 mL:
200 µL Eppendorf tip (yellow)



Cylinder volumes 20 and 50 mL:
1000 µL Eppendorf tip (blue)



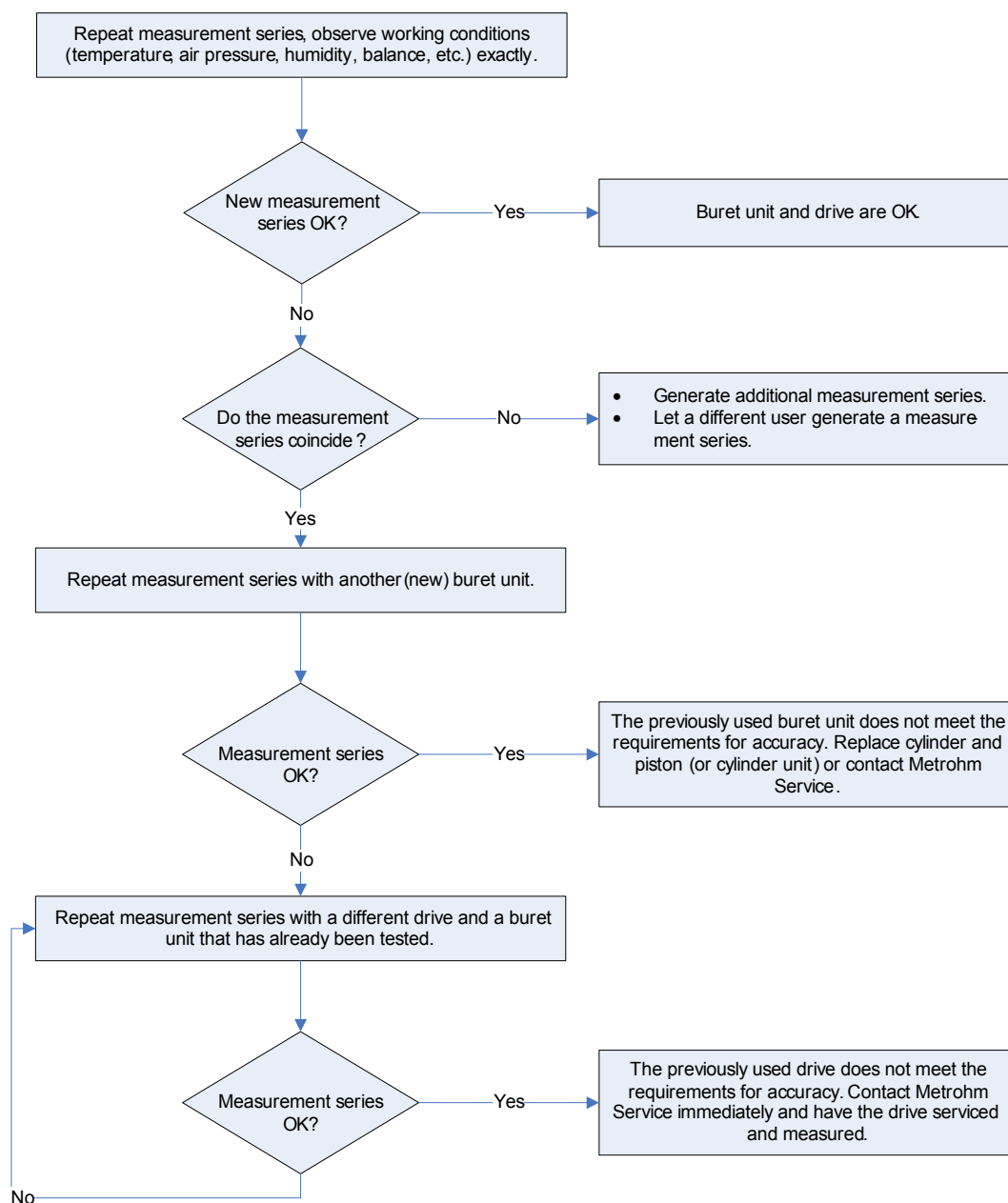
2. Troubleshooting flowchart: What must be done if the values do not meet the specified criteria?

You yourself must define the limit values within which your results must lie in accordance with the requirements of your particular application. The given values are proposed by Metrohm as guide values; they are binding according to ISO 8655-3. Please consult the Instructions for use of your Dosing or Exchange Unit.

Procedure if the values are outside the limits:

- Check whether the tubing and tubing connections of the buret unit are leaking.
- Check the accuracy of the balance used.
- Check the measured values of your environmental parameters. Are the following correct: air pressure, temperature, relative humidity, density of the balance calibration weight, etc.?
- Have all the instruments used been acclimatized to the room temperature for at least 2 h?
- Clean/service the buret unit according to the Instructions for use.

If everything seems to be OK:



3.1 Test report for the validation of a 20 mL Dosing Unit (page 1)

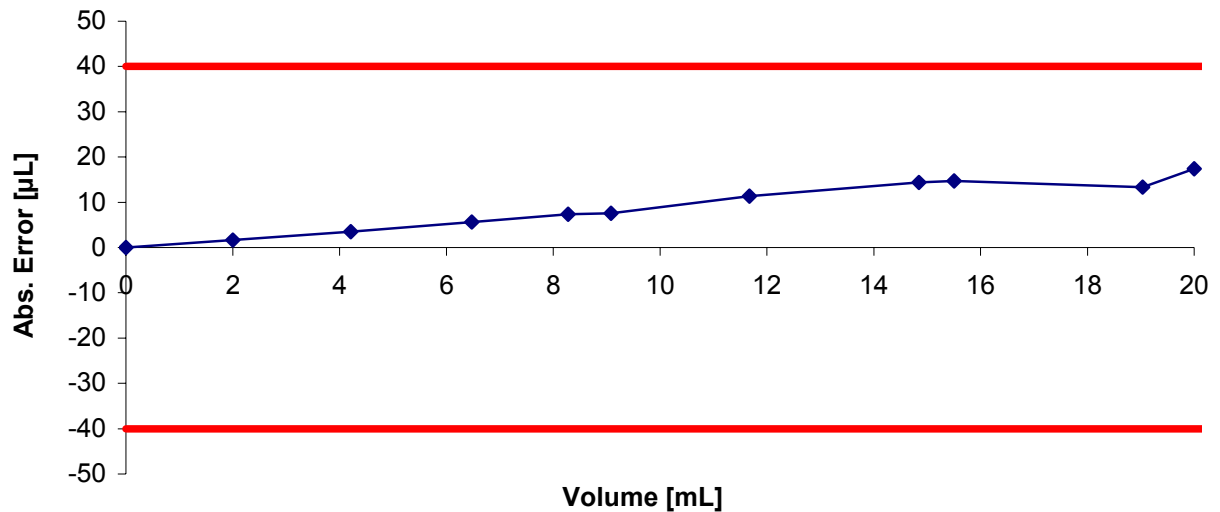
Linearity test for Metrohm burets

Metrological performance test of volumetric apparatus - Gravimetric method

System components:

Buret unit:	DU20	Cylinder type:	6.1571.220
Buret type:	DU	Nominal volume:	20 mL Ex / 20 °C
Serial number:	10680591	Cylinder serial number:	767
Instrument ID:	1.809.0010	Location:	Chem. Lab. 1b
Model:	Titrande 809	Program version:	8090005
Serial number:	2186	Dosing drive:	E1: Dosino 800
Drive ID:	1.800.0010	Balance ID:	XR 305A
Type of drive:	Dosino 800	Balance model:	Precisa
Serial number:	2288	Serial number:	3289532838
Temperature:	22.60 °C	Density of liquid:	0.997629 g/mL
Barom. pressure:	927 mbar	Calculation factor:	1.003338
Density cal. weight:	8.0000 g/mL	Dosing rate:	66.00 mL/min
Air density:	0.001093 g/mL	Dosing mode:	repetitive

Results:



Slope	1.001	1.000 +/- 0.003	passed
Abs. Error _{at nominal volume of cylinder}	17.4	µL	passed

Assessment: This unit has passed the test.

Date: 13.07.2004
 Time: 16:52 Uhr

Operator: B.Christensen

Signature: 

3.2 Test report for the validation of a 20 mL Dosing Unit (page 2)

Linearity test for Metrohm burets

Metrological performance test of volumetric apparatus - Gravimetric method

Auxiliaries:

Thermometer ID: 64691_1
 Model: 628.0015
 Supplier: Testo

Barometer ID: 64691_2
 Model: 638.1645
 Supplier: Testo

Dosing tip ID: 1000 µL Tip
 Model: Tip blue
 Supplier: Eppendorf

Test liquid: Water
 Concentration: -
 Supplier: -

Results:

Test volume V_s [mL]	Mass m_i [g]	Volume _{act} V_i [mL]	Error _(abs.) E_{abs} [µL]
2.000	1.995	2.0017	1.66
4.212	4.202	4.2155	3.52
6.474	6.458	6.4797	5.65
8.280	8.260	8.2874	7.37
9.082	9.059	9.0895	7.54
11.674	11.647	11.6854	11.37
14.850	14.815	14.8643	14.34
15.508	15.471	15.5227	14.73
19.036	18.986	19.0494	13.37
20.000	19.951	20.0174	17.39

Balance report:

	Reading	Mass	Time/Comment
m_0	56.4321		none
m_1	58.4271	1.9950	none
m_2	62.6286	4.2015	none
m_3	69.0867	6.4581	none
m_4	77.3465	8.2598	none
m_5	86.4058	9.0593	none
m_6	98.0523	11.6465	none
m_7	112.8672	14.8149	none
m_8	128.3383	15.4711	none
m_9	147.3243	18.9860	none
m_{10}	167.2751	19.9508	none