

Comparison of primary standards for liquid micro flow rates

EURAMET project 1291

EURAMET Regional Supplementary Comparison

EURAMET.M.FF-S7



Pilot

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1 Introduction

An intercomparison has been organized with the purpose to determine the degree of equivalence of several newly developed primary standards for liquid flow rates from 0.12 g/h up to 200 g/h (equivalent with 2 $\mu\text{l}/\text{min}$ to 3.3 ml/min). This intercomparison is the first one for such low flow rates in Europe at NMI level. The operating conditions are ambient pressure and temperature.

The development of (most of) the primary standards as well as this intercomparison is part of the MeDD project [3]. Hence, the ultimate goal is to validate the claimed uncertainties of the developed primary standards.

This intercomparison was initialized as a EURAMET research project (project 1291), however later was upgraded to become a EURAMET supplementary comparison in the scope of the BIPM, EURAMET.M.FF-S7.

This report discusses the protocol as well as the results following the intercomparison. It is organized as follows. Section 2 gives the participants and followed time schedule. Section 3 discusses the transfer standards used, whereas Section 4 discusses the protocol used. Next, Section 5 discusses the results which are evaluated in Section 6. Finally, in Section 7 the conclusion is drawn.

2 Participants and time schedule

For the intercomparison two different transfer standards have been used: a Coriolis flow meter and a syringe pump (flow generator). Both a flow meter and a flow generator have been used to validate the standards for the two different calibration principles. Further, two different types of transfer standards minimizes the risk of making the same systematic errors. In Table 1 the participants for the syringe pump intercomparison are shown, whereas the participants for the flow meter intercomparison are shown in Table 2. MIKES and FH Lübeck only participated for the syringe pump because of limited possibilities to calibrate flow meters. Each time the two transfer standards have been sent together to the next lab.

The flow meter intercomparison consists of 3 rounds. For the first round the following labs participated: DTI, IPQ, LNE-CETIAT and METAS. The second round is formed by supplementary partners to the first round (Bronkhorst High-Tech and VSL). The third round includes all partners, however different flow points. In Table 2 the 'id' reflects the round and number within that round.

The tables show several time gaps. This is because several labs initially had issues with performing the calibrations which caused delays. Also there has been one major delay at one of the customs.

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Table 1 Participants syringe pump intercomparison. Between square brackets the abbreviation if used and between parentheses the country.

| id | Laboratory (country) | Contact Person | Date | remarks |
|----|--|-------------------|--------------------------------|--|
| 1 | METAS (Switzerland) | Hugo Bissig | November 2013 to December 2013 | Start intercomparison by pilot, flow points 2 µl/min to 333 µl/min |
| 2 | DTI (Denmark) | Claus Melvad | January 2014 | Calibration by partner, flow points 2 µl/min to 333 µl/min |
| 3 | FH Lübeck [FH L] (Germany) | Martin Ahrens | February 2014 | Calibration by partner, flow point 1 µl/min |
| 4 | VSL (Netherlands) | Harm Tido Petter | April 2014 | Calibration by partner, flow points 2 µl/min to 333 µl/min |
| 5 | IPQ (Portugal) | Elsa Batista | May 2014 | Calibration by partner, flow points 2 µl/min to 333 µl/min, new 2.5 ml syringe |
| 6 | MIKES (Finland) | Hannu Sairanen | June 2014 | Calibration by partner, flow points 2 µl/min and 10 µl/min |
| 7 | Bronkhorst High-Tech [BHT] (Netherlands) | Joost Lötters | October 2014 to November 2014 | Calibration by partner, flow points 2 µl/min to 333 µl/min, new 2.5 ml syringe |
| 8 | LNE-CETIAT [CETIAT] (France) | Florestan Ogheard | December 2014 | Calibration by partner, flow points 2 µl/min to 333 µl/min |
| 9 | METAS (Switzerland) | Hugo Bissig | January 2015 | Closure by pilot |

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Table 2 Participants Coriolis flow meter intercomparison. Between square brackets the abbreviation if used and between parentheses the country.

| id | Laboratory (country) | Contact Person | Date | remarks |
|-----|--|-------------------|---------------------------------|--|
| 1-1 | LNE-CETIAT [CETIAT] (France) | Christopher David | August 2012 to September 2012 | Start intercomparison by pilot, flow points 2 g/h to 200 g/h |
| 1-2 | DTI (Denmark) | Claus Melvad | September 2012 to November 2012 | Calibration by partner, flow points 2 g/h to 200 g/h |
| 1-3 | METAS (Switzerland) | Hugo Bissig | November 2012 to December 2012 | Calibration by partner, flow points 2 g/h to 200 g/h |
| 1-4 | IPQ (Portugal) | Elsa Batista | January 2013 | Calibration by partner, flow points 2 g/h to 200 g/h |
| 1-5 | LNE-CETIAT [CETIAT] (France) | Christopher David | February 2013 | Reproducibility check by pilot, flow points 2 g/h to 200 g/h |
| 1-6 | METAS (Switzerland) | Hugo Bissig | June 2013 | Reproducibility check by participant, flow points 2 g/h to 200 g/h |
| 2-1 | Bronkhorst High-Tech [BHT] (Netherlands) | Joost Lötters | July 2013 to Augustus 2013 | Calibration by supplementary partner, flow points 2 g/h to 200 g/h |
| 2-2 | VSL (Netherlands) | Harm Tido Petter | September 2013 to December 2013 | Calibration by supplementary partner, flow points 60 g/h and 200 g/h |
| 3-1 | DTI (Denmark) | Claus Melvad | January 2014 | Start second round, flow points 0.5 g/h and 2 g/h. Adjusted flow curve |
| 3-2 | IPQ (Portugal) | Elsa Batista | May 2014 | Calibration by partner, flow points 0.5 g/h and 2 g/h |
| 3-3 | METAS (Switzerland) | Hugo Bissig | June 2014 | Calibration by partner, flow points 0.5 g/h and 2 g/h |
| 3-4 | Bronkhorst High-Tech [BHT] (Netherlands) | Joost Lötters | October 2014 to November 2014 | Calibration by partner, flow points 0.5 g/h and 2 g/h |
| 3-5 | LNE-CETIAT [CETIAT] (France) | Florestan Ogheard | December 2014 | Calibration by partner, flow points 2 g/h to 200 g/h |
| 3-6 | VSL (Netherlands) | Harm Tido Petter | December 2014 to January 2015 | Calibration by partner, flow points 0.5 g/h to 200 g/h |

3 Transfer standards

3.1 Syringe pump

For the flow generator, the Nexus Syringe pump 3000 from *Chemyx*[®] (serial number 2172176) has been used, see Figure 1. The syringes were of the type H-TLL with a PTFE seal (manufacturer ILS Innovative Labor System GmbH).

This syringe pump has been chosen because the delivered pulsations were believed of the lowest magnitude. However, during the intercomparison it was found the pulsations are not negligible; hence a special procedure had to be adopted to make sure the flow rate pulsations did not influence the results (discussed in Section 4.3.1).



Figure 1 *Chemyx*[®] Nexus 3000 syringe pump.

3.2 Coriolis flow meter

For the flow meter a Coriolis flow meter from *Bronkhorst High-Tech*[®] has been used (ref: M12P-AGP-11-0-5; S/N: B12200826A), see Figure 2. Together with the flow meter 1/8" stainless steel tubing and fast connecting valves from Upchurch were used. The transfer standard has been transported only by road to avoid the possible impact on the flow meter curve by low pressure during air transport.



Figure 2 Coriolis flow meter including mass block from *Bronkhorst High-Tech*.

During the intercomparison the flow meter was measured more than once by various labs, in particular:

- LNE-CETIAT had to redo all measurements because the first results (1.1 and 1.5 from Table 2) were significantly off compared to the other labs. Hereafter LNE-CETIAT made various modifications to the set up.
- VSL had to redo most measurements because a mass flow controller (part of the setup) was damaged (2.2 from Table 2) which limited the flow rate.
- Most labs calibrated the flow meter for 2 g/h twice.

In order to make sure that the participants never had prior information on the expected flow meter error, the calibration curve of the meter was changed after the first round including supplement (1.1 to 2.2 in Table 2). The calibration curve was modified by changing the sensitivity of the Coriolis flow meter. This has resulted in a -0.63% change for the flow meter deviation for all flow points. Hence, when errors of the third round (3.1 to 3.6) are compared to the first and supplement (1.1 tot 2.2), the flow rater error is superimposed with +0.63%. In all subsequent results this shift has already been made.

4 Measurement procedure

4.1 Measured quantity

The intercomparison is based on comparing the relative error of the transfer standards as determined by the participating labs. The relative error ε (%) is defined as:

$$\varepsilon = 100 \frac{q_{indicated} - q_{ref}}{q_{ref}} \quad (1)$$

where $q_{indicated}$ is the indicated flow rate by the flow meter or the set point of the syringe pump and q_{ref} is the reference flow rate. For the syringe pump the volumetric flow rate is taken, whereas the mass flow rate for the Coriolis flow meter is used.

4.2 Facilities

The participating National Metrology Institutes (NMI) used their own calibration procedures to calibrate the flow meter and syringe pump. In Table 3 an overview is given of the participating laboratories, the type of facility, calibration procedure and references for further reading if existing. All laboratories are independent, however Bronkhorst High-Tech and FH Lübeck do not contribute to the RV (reference value) because these labs are not an NMI or DI (Designated Institute).

Table 3 Overview participating laboratories, type of facility, calibration procedure and references for further reading if existing.

| Laboratory (country) | Facility type | Calibration procedure | Further reading |
|----------------------|--|-------------------------------------|-----------------|
| Bronkhorst High-Tech | Gravimetric, submerged dispensing needle, layer of oil on top of the water surface to avoid evaporation | Dynamic | [2], [5] |
| DTI | Gravimetric, submerged dispensing needle, layer of oil on top of the water surface to avoid evaporation | Dynamic | [2] |
| CETIAT | Gravimetric, submerged dispensing needle, nearly saturated air around beaker to avoid evaporation | Start/ stop | [2] |
| FH Lübeck | Front tracking of a moving meniscus in a capillary of known dimensions | Start/ stop | [1] |
| IPQ | Gravimetric, submerged dispensing needle, nearly saturated air around beaker to avoid evaporation | Dynamic (pooled standard deviation) | [2], [3] |
| METAS | Gravimetric, continuous water flow by means of water bridge of 50 μm from dispensing needle to fast water absorbing material in beaker, nearly saturated air around beaker and fast water absorbing material to avoid evaporation | Dynamic | [2] |
| MIKES | Gravimetric, not submerged dispensing needle, nearly saturated air near balance to avoid evaporation | Dynamic | N/A |
| VSL | Gravimetric, submerged dispensing needle, nearly saturated air around beaker to avoid evaporation | Dynamic | [2] |

4.3 Calibration protocol and measurement conditions

In this section the calibration protocol is described and the (range of) measurement conditions are given. A distinction is made for the syringe pump and flow meter.

4.3.1 Syringe pump

The following (range of) measurement conditions has been used:

- Water temperature between 20 °C and 23 °C.
- The measurement time follows from the start/ end position and plunger velocity.
- A minimum of 3 repetitions.
- Flow rates: 2 $\mu\text{l}/\text{min}$, 10 $\mu\text{l}/\text{min}$, 33 $\mu\text{l}/\text{min}$, 100 $\mu\text{l}/\text{min}$ and 333 $\mu\text{l}/\text{min}$. Note, in case a lab could not cover the whole range, a selection of flow points was made, see also Table 1.

The following procedure has been used to calibrate the syringe pump:

- After receiving the syringe pump visually inspect it for damages and whether the package is complete. If all looks well install the syringe pump in the horizontal plane. Perform leak tests and make sure the installation is water tight.
- Fill the syringe for which the measurement will be performed. Each lab used their method; however special care has been taken to have a syringe filled with fully degassed water.
- Mount the syringe on the syringe pump and set the plunger at the plunger starting position. Manually empty the syringe until the syringe is at the start position (see Table 4). Set the following parameters: the volume to be dispensed, the flow rate and the diameter of the glass syringe used (see Table 4). The dispensed volume and analyzed volume is such that an integer amount of cycles is performed by the syringe pump.
- Calibrate the syringe pump using the laboratory calibration procedure and determine the flow rate error as defined in Section 4.1.

Table 4 Syringe volumes, dispensed volume and flow rates. The dispensed volume and analyzed volume is such that an integer amount of cycles is performed by the syringe pump.

| Flow rate (µl/min) | Syringe volume (µl) | Inner diameter (mm) | # of cycles (-) | start position (µl) | dispensed volume (µl) | position used for data analyses (µl) | meas. time (min) |
|--------------------|---------------------|---------------------|-----------------|---------------------|-----------------------|--------------------------------------|------------------|
| 2 | 2500 | 7.28 | 2 | 800 | 300 | 700 to 575 | 150 |
| 10 | 2500 | 7.28 | 4 | 800 | 600 | 600 to 575 | 60 |
| 33 | 5000 | 10.30 | 4 | 2000 | 1500 | 1400 to 900 | 45 |
| 100 | 25000 | 23.03 | 3 | 8000 | 3000 | 7300 to 5400 | 30 |
| 333 | 25000 | 23.03 | 3 | 8000 | 3000 | 7300 to 5400 | 9 |

4.3.2 Flow meter

The following (range of) measurement conditions has been used:

- Upstream pressure: 0.5 to 2.5 bar depending on the required flow rate.
- Water temperature between 20 °C and 23 °C.
- Minimal measurement time depends on the set up, however sufficient to have a stable flow over at least one minute.
- A minimum of 3 repetitions.
- Flow rates: 0.5 g/h, 2 g/h, 6 g/h, 20 g/h, 60 g/h and 200 g/h. Note 1, in case a lab could not cover the whole range, a selection of flow points was made, see also Table 2. Note 2, some labs performed (some of) the measurements at a later stage than the other flow points, see also Table 2.

The following procedure has been used to calibrate the flow meter:

- After receiving the flow meter visually inspect the meter for damages and whether the package is complete. If all looks well install the meter in the horizontal plane and turn it on. Perform leak tests and make sure the installation is water tight.
- Purge the meter with fully degassed and pure water (demineralized, or single/ double distilled water). Purge sufficiently long to make sure there is no dissolved and entrapped air upstream of the flow meter and between the meter and the measurement beaker. For this particular flow meter a good check is to quickly open and close a valve just up and downstream of the meter. In case the flow meter jumps to zero and back within 0.5 seconds, the system is typically properly degassed. Note, some labs pre-primed the system with CO₂ gas or created a (near) vacuum downstream of the meter as this sometimes helps in a quicker degasification.
- For the flow rate at hand, wait for stable temperature conditions. At stable conditions, create zero flow rate and ambient pressure. Zero the flow meter.
- Calibrate the flow meter using the laboratory calibration procedure and determine the flow rate error as defined in Section 4.1.

5 Measurement results

5.1 Stability of the transfer standards

5.1.1 Syringe pump

The stability of the syringe pump has been checked by the pilot lab for the syringe pump. Hereto, the pilot determined the error at the beginning and the end of the intercomparison for two series of syringes. The second series has been used for the intercomparison, whereas the first one was intended as back up. The calibration results for the second series are shown in Table 5.

Unfortunately, the syringe with a volume of 2.5 ml was broken and consequently replaced twice during the intercomparison. Hence, for this syringe volume the reproducibility cannot be determined by comparing the initial values with the final values. Therefore, for this syringe volume the reproducibility is estimated by comparing all calibration data available, see Table 6.

The uncertainty due to drift follows from the difference in measured error by assuming a uniform distribution. Hence,

$$u_{drift} = \frac{\Delta\varepsilon}{2\sqrt{3}} \quad (2)$$

where u_{drift} ($k=1$) is the uncertainty due to drift (reproducibility) and $\Delta\varepsilon$ is the difference in measured error at the beginning and end of the intercomparison (or the maximum difference for the syringe volume of 2.5 ml).

Table 5 Reproducibility for the syringe volumes 5 and 25 ml (second series of syringes).

| target flow rate (µl/min) | syringe volume (ml) | start of intercomparison | | end of intercomparison | | reproducibility | |
|---------------------------|---------------------|--------------------------|----------------|------------------------|----------------|-----------------|--------------------------|
| | | error (%) | sample std (%) | error (%) | sample std (%) | Δ error (%) | U _{drift} (k=2) |
| 33 | 5 | 0.11 | 0.18 | 0.25 | 0.13 | 0.13 | 0.08 |
| 100 | 25 | -0.13 | 0.19 | -0.09 | 0.16 | 0.04 | 0.02 |
| 333 | 25 | 0.1 | 0.07 | -0.28 | 0.18 | 0.39 | 0.22 |

Table 6 Estimated reproducibility for the syringe volume of 2.5 ml based on measurements for the 1st, 2nd and 3rd series of syringes.

| target flow rate (µl/min) | syringe series 2, start intercomparison | | syringes series 1, start intercomparison | | syringe series 3, end intercomparison | | estimated reproducibility | |
|---------------------------|---|----------------|--|----------------|---------------------------------------|----------------|---------------------------|--------------------------|
| | error (%) | sample std (%) | error (%) | sample std (%) | error (%) | sample std (%) | max Δ error (%) | U _{drift} (k=2) |
| 2 | -1.98 | 0.04 | -1.35 | 0.07 | -1.96 | 0.52 | 0.64 | 0.36 |
| 10 | -0.11 | 0.24 | -0.01 | 0.02 | -0.38 | 0.02 | 0.36 | 0.20 |

The uncertainty due to the drift is added (quadratically) to the calibration uncertainty (uncertainty in reference flow rate and the repeatability which is defined as the sample standard deviation divided by the square root of the number of repetitions). Another approach to treat the uncertainty due to drift is to include it only in the uncertainty of the reference value and in the determination of the degree of equivalence (E_n value). However, when the uncertainty due to drift is small compared to the calibration uncertainty, both approaches give similar results (which is typically the case for a carefully selected transfer standard).

5.1.2 Flow meter

The stability of the flow meter could not be checked by the pilot lab because their initial results were off compared to the other results. Therefore, the drift (reproducibility) of the meter is assessed by looking at repeated measurement series from other labs. Bronkhorst High-Tech and METAS both repeated (a part of) the flow points during the inter comparison, see Table 7. The maximum difference in the determined error is subsequently compared to the zero stability of the meter in Table 8.

From Table 8 it follows the flow meter error does not significantly fluctuate more than the specified (by manufacturer) zero stability of the meter except for a flow rate of 200 g/h. In order to be on the safe side (the reproducibility was not checked by a pilot lab, however in between partners), the worst case of the zero stability and reproducibility has been used to determine the uncertainty due to drift. Nevertheless, the uncertainty due to drift is small and except for the lowest two flow points smaller than twice the calibration uncertainty.

Table 7 Repeated measurement results from two different laboratories.

| target flow rate (g/h) | Bronkhorst High-Tech | | | METAS | | | VSL | | | max Δ (%) |
|------------------------|----------------------|----------------------|--------------|----------------------|----------------------|--------------|----------------------|----------------------|--------------|------------------|
| | error 1st series (%) | error 2nd series (%) | Δ (%) | error 1st series (%) | error 2nd series (%) | Δ (%) | error 1st series (%) | error 2nd series (%) | Δ (%) | |
| 2 | -0.55 | -0.85 | 0.31 | - | - | - | - | - | - | 0.31 |
| 6 | -0.23 | -0.38 | 0.15 | -0.51 | -0.40 | 0.11 | - | - | - | 0.24 |
| 20 | -0.14 | -0.21 | 0.07 | -0.09 | -0.32 | 0.24 | - | - | - | 0.07 |
| 60 | - | - | - | -0.18 | -0.14 | 0.04 | -0.17 | -0.20 | 0.03 | 0.04 |
| 200 | - | - | - | -0.18 | -0.14 | 0.04 | -0.13 | -0.06 | 0.07 | 0.07 |

Table 8 Maximum difference flow meter error, zero stability and uncertainty due to drift.

| target flow rate (g/h) | max difference (%) | zero stability (%) | uncertainty due to drift ($k=2$) (%) |
|------------------------|--------------------|--------------------|--|
| 0.5 | - | 4.0 | 2.31 |
| 2 | 0.31 | 1.0 | 0.58 |
| 6 | 0.24 | 0.33 | 0.19 |
| 20 | 0.07 | 0.10 | 0.06 |
| 60 | 0.04 | 0.03 | 0.02 |
| 200 | 0.07 | 0.01 | 0.04 |

5.1.3 Flow meter versus flow generator

In Table 9 the uncertainty due to drift for the syringe pump and flow meter is given. From this table it follows that the syringe pump is a better choice for the lower flow rates. This is as expected because the zero stability of the flow meter becomes limiting for flow rates below of 2 g/h and lower.

Table 9 Comparison reproducibility flow meter and syringe pump. The flow rates without parentheses are performed points, flow rates between parentheses only give the equivalent of the volumetric or mass flow rate.

| target flow rate (g/h) | target flow rate ($\mu\text{l}/\text{min}$) | uncertainty due to drift syringe pump ($k=2$) (%) | uncertainty due to drift flow meter ($k=2$) (%) |
|------------------------|---|---|---|
| (0.12) | 2 | 0.36 | |
| 0.5 | 8 | | 2.31 |
| (0.6) | 10 | 0.20 | |
| 2 | 33 | 0.08 | 0.58 |
| 6 | 100 | 0.02 | 0.19 |
| 20 | 333 | 0.22 | 0.06 |
| 60 | (1000) | | 0.02 |
| 200 | (3333) | | 0.04 |

5.2 Laboratory results

5.2.1 Syringe pump

In Table 10 the calibration results of the participating labs for the syringe pump are shown. The flow rate of 1 µl/min was not officially part of the protocol, however this was the highest flow rate FH Lübeck could achieve at that time and therefore it is listed in the table as well. IPQ has changed the value for 10 µl/min after draft A was released. The original value led to a warning, however was discarded because the average included measurements that likely were influenced by air bubbles (first measurement).

According to Table 10 the flow rate error can be different for the same syringe volume, however different flow rate. This is because the flow rate error is a function of the inner diameter of the syringe and the plunger velocity. Since the error of the plunger velocity can depend on the velocity, also the flow rate error can depend on the flow rate itself.

Table 10 Error (%) as determined by the participating labs for the syringe pump

| flow rate (µl/min) | syringe volume (ml) | BHT | CETIAT | DTI | IPQ | FH L | METAS | MIKES | VSL |
|--------------------|---------------------|-------|--------|-------|-------------------|------|-------|-------|-------|
| 1 | 2.5 | - | - | - | - | 0.02 | - | - | - |
| 2 | 2.5 | -1.42 | -1.08 | -1.45 | -2.35 | - | -1.98 | -0.01 | -1.64 |
| 10 | 2.5 | 0.03 | -0.22 | 0.32 | 0.37 ¹ | - | -0.11 | 0.00 | -0.02 |
| 33 | 5 | 0.23 | -0.04 | 0.11 | 0.74 | - | 0.08 | - | 0.46 |
| 100 | 25 | -0.04 | -0.19 | 0.07 | -0.01 | - | -0.13 | - | 0.07 |
| 333 | 25 | -0.16 | -0.31 | -0.11 | -0.12 | - | 0.11 | - | -0.09 |

1) Value changed after Draft A was released (original value is 0.61).

5.2.2 Flow meter

In Table 11 the calibration results of the participating labs for the flow meter are shown. As mentioned earlier, some labs performed measurements for one or more flow points more than once. In case there are multiple results for one flow point by one lab, the most recent measurements have been used for the analyses. One could argue to take an average in case there are multiple values, however as this is not common practice when calibrating a device under test, this approach is also not adopted here.

Table 11 Error (%) as function of the indicated flow rate as determined by the participating labs for the flow meter.

| target flow rate (g/h) | BHT | | CETIAT | | DTI | | IPQ | | METAS | | VSL | |
|------------------------|----------------------|-----------|----------------------|-----------|----------------------|-----------|----------------------|-----------|----------------------|-----------|----------------------|-----------|
| | ind. flow rate (g/h) | error (%) |
| 0.5 | 0.5 | -1.65 | 0.57 | -1.96 | 0.58 | -2.40 | 0.49 | -0.19 | - | - | 0.46 | 0.71 |
| 2 | 2 | -0.85 | 2.14 | -1.01 | 2.06 | -0.90 | 1.94 | 0.07 | 2.13 | -0.40 | 1.93 | -0.30 |
| 6 | 6 | -0.38 | 6.01 | -0.55 | 6.03 | -0.46 | 6.20 | 0.03 | 6.55 | -0.32 | 5.94 | -0.20 |
| 20 | 20 | -0.21 | 20.8 | -0.25 | 20.1 | -0.21 | 19.8 | -0.01 | 19.8 | -0.14 | 19.8 | -0.15 |
| 60 | 60 | -0.16 | 60.7 | -0.30 | 60.4 | -0.17 | 62.9 | -0.15 | 64.1 | -0.14 | 59.5 | -0.10 |
| 200 | 200 | -0.17 | 196 | -0.38 | 197.6 | -0.16 | 198 | -0.18 | - | - | 198 | -0.06 |

For METAS the second last series is used for the intercomparison because the results from the last series are assumed to be outliers. This is because METAS performed this measurement series too much in a hurry. As a result, the flow meter had been improperly zeroed leading to untrustworthy results.

5.3 Uncertainty

5.3.1 Calibration uncertainty for syringe pump flow points

In Table 12 and Table 13 the calibration uncertainty ($k=2$) for the syringe pump is given. Table 12 gives the calibration uncertainty including the uncertainty in reference flow rate and repeatability (sample standard deviation of the various repetitions divided by the square root of the number of repetitions), whereas in the uncertainties given in Table 13 also the uncertainty due to the drift is included.

Table 12 Calibration uncertainty syringe pump as obtained by the various labs.

| flow rate (µl/min) | BHT | CETIAT | DTI | IPQ | FH L | METAS | MIKES | VSL |
|--------------------|------|--------|------|------|------|-------|-------|------|
| 1 | - | - | - | - | 3.46 | - | - | - |
| 2 | 5.05 | 0.87 | 1.45 | 0.87 | - | 0.68 | 4.20 | 2.29 |
| 10 | 1.03 | 0.63 | 4.18 | 0.61 | - | 0.31 | 3.00 | 0.93 |
| 33 | 0.36 | 0.65 | 1.35 | 0.58 | - | 0.24 | - | 0.35 |
| 100 | 0.17 | 0.61 | 3.17 | 0.24 | - | 0.26 | - | 0.24 |
| 333 | 0.07 | 0.10 | 1.25 | 0.31 | - | 0.27 | - | 0.29 |

Table 13 Calibration uncertainty including drift syringe pump for the various labs. The value for FH Lübeck does not include a term for drift because it is unknown for this flow rate.

| flow rate (µl/min) | BHT | CETIAT | DTI | IPQ | FH L | METAS | MIKES | VSL |
|--------------------|------|--------|------|------|------|-------|-------|------|
| 1 | - | - | - | - | 3.46 | - | - | - |
| 2 | 5.06 | 0.94 | 1.49 | 0.95 | - | 0.77 | 4.22 | 2.32 |
| 10 | 1.05 | 0.66 | 4.18 | 0.65 | - | 0.37 | 3.01 | 0.95 |
| 33 | 0.37 | 0.66 | 1.35 | 0.59 | - | 0.25 | - | 0.36 |
| 100 | 0.17 | 0.61 | 3.17 | 0.25 | - | 0.26 | - | 0.24 |
| 333 | 0.23 | 0.25 | 1.27 | 0.38 | - | 0.35 | - | 0.37 |

5.3.2 Calibration uncertainty for flow meter flow points

In Table 14 and Table 15 the calibration uncertainty ($k=2$) for the flow meter is given. Table 14 gives the calibration uncertainty including the uncertainty in reference flow rate and repeatability, whereas in Table 15 also the uncertainty due to drift is included.

Table 14 Calibration uncertainty flow meter as obtained by the various labs.

| flow rate (g/h) | BHT | CETIAT | DTI | IPQ | METAS | VSL |
|-----------------|------|--------|------|------|-------|------|
| 0.5 | 1.20 | 0.61 | 2.07 | 0.94 | - | 0.67 |
| 2 | 0.31 | 0.62 | 0.52 | 0.62 | 0.20 | 0.21 |
| 6 | 0.12 | 0.62 | 0.69 | 0.39 | 0.12 | 0.10 |
| 20 | 0.06 | 0.10 | 0.22 | 0.28 | 0.12 | 0.10 |
| 60 | 0.06 | 0.10 | 0.09 | 0.27 | 0.13 | 0.10 |
| 200 | 0.10 | 0.10 | 0.07 | 0.27 | - | 0.05 |

Table 15 Calibration uncertainty including drift flow meter for the various labs.

| flow rate (g/h) | BHT | CETIAT | DTI | IPQ | METAS | VSL |
|-----------------|------|--------|------|------|-------|------|
| 0.5 | 2.60 | 2.39 | 3.10 | 2.49 | - | 2.40 |
| 2 | 0.66 | 0.83 | 0.78 | 0.85 | 0.61 | 0.61 |
| 6 | 0.23 | 0.63 | 0.72 | 0.43 | 0.23 | 0.22 |
| 20 | 0.08 | 0.12 | 0.23 | 0.29 | 0.13 | 0.12 |
| 60 | 0.06 | 0.10 | 0.09 | 0.27 | 0.13 | 0.10 |
| 200 | 0.10 | 0.10 | 0.07 | 0.27 | - | 0.05 |

6 Evaluation

In this section the results are evaluated. Key of this evaluation is to study whether the calibration results of the various labs are consistent with each other. To judge whether the results are consistent the well-known E_n is used. This value is defined as:

$$E_{nlab-i} = \frac{\varepsilon_{lab-i} - \varepsilon_{RV}}{\sqrt{U^2(\varepsilon_{lab-i}) - U^2(\varepsilon_{RV})}} \quad (3)$$

where ε_{lab-i} is the error of lab- i for a certain flow point, ε_{RV} is the comparison reference value (RV) for the error and $U(\varepsilon_{lab-i})$ and $U(\varepsilon_{RV})$ are the expanded uncertainties ($k=2$) of those values. The (expanded) uncertainty includes the uncertainty in reference flow rate, repeatability and the reproducibility (see Section 5.1). The repeatability is defined as the sample standard deviation divided by the square root of the number of repetitions. Remark, one lab uses the pooled standard deviation rather than the sample standard deviation (see also Table 3).

The value of E_n has the following meaning:

- The results of a laboratory for a certain flow point are consistent (passed) if $E_n \leq 1$.
- The results of a laboratory for a certain flow point are inconsistent (failed) if $E_n > 1.2$.
- For results between $1 < E_n \leq 1.2$ a "warning level" is defined. For this particular situation the particular lab is recommended to check the procedures and methodology.

The comparison reference value is the uncertainty weighted average of the error and is determined as follows:

$$\varepsilon_{RV} = \frac{\sum_{i=1}^n \varepsilon_{lab-i} / U^2(\varepsilon_{lab-i})}{\sum_{i=1}^n 1 / U^2(\varepsilon_{lab-i})} \quad (4)$$

where n is the number of participating labs. The uncertainty of the RV follows from:

$$u(\varepsilon_{RV}) = \frac{1}{\sqrt{\sum_{i=1}^n 1 / U^2(\varepsilon_{lab-i})}} \quad (5)$$

Finally, the chi-squared test is applied to see whether the determined errors and accompanying uncertainties can be expected based on a Gaussian distribution. If so, the reference value can be accepted. The chi-squared test is defined as follows, for each flow point, chi-squared is defined as:

$$\chi_{obs}^2 = \sum_{i=1}^n \left(\frac{\varepsilon_{lab-i} - \varepsilon_{RV}}{u(\varepsilon_{lab-i})} \right)^2 \quad (6)$$

Note, here $u(\varepsilon_{lab-i})$ is the standard uncertainty ($k=1$). The set of measurement results for a certain flow point is only accepted when:

$$Pr(\chi^2(n-1) > \chi_{obs}^2) < 0.05 \quad (7)$$

where Pr stands for probability and $\chi(n)$ is the expected value for a Gaussian distribution. Using the CHIINV(probability, degrees of freedom-1) function from Excel, this can be rewritten as follows for a consistent set (coverage factor 95%):

$$\chi_{obs}^2 < CHIINV(0.05; n-1) \quad (8)$$

Hence, if the observed chi-squared value satisfies the above equation, the reference value is accepted. If not, the result with the largest contribution to χ_{obs}^2 is discarded and the test is repeated (degrees of freedom reduced by one).

6.1 Syringe pump

In Figure 3 the calibration results of all labs for the syringe pump are shown. The plotted flow rates have been given an artificial offset in order to visualize the results. For example, the last series of measurements all have an indicated flow rate of 333 $\mu\text{l}/\text{min}$.

The uncertainty in Figure 3 include the uncertainty in reference flow rate, repeatability and the drift (see Section 5.1.1). Next, in Table 16 the E_n value is given, whereas in Table 17 the reference values (equation (4)) and uncertainties (equation (5)) are given. Finally, in Table 18 the results for the chi-squared tests are given (following equations (6) and (8)). First, from Table 18 it follows that the reference value can be accepted. Next, from Figure 3 and Table 16 it follows all results are consistent.

The results from FH Lübeck cannot directly be compared with the other results because of a mismatch in flow rate. This is in particular the case because the flow rate error depends on the flow rate. Would the flow rate error for 1 $\mu\text{l}/\text{min}$ and 2 $\mu\text{l}/\text{min}$ be similar, the results from FH Lübeck are consistent as well.

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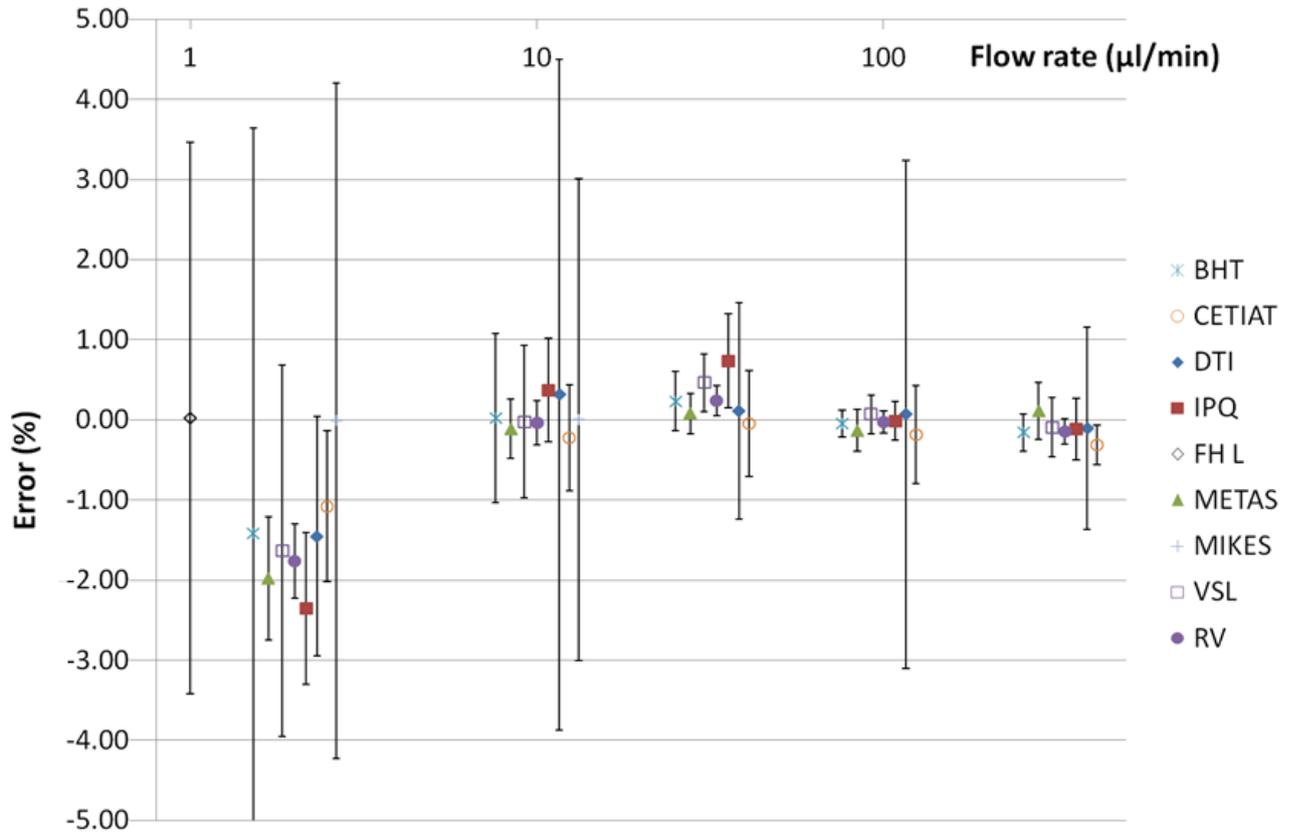


Figure 3 Results intercomparison for the syringe pump (artificial offset flow rate for visibility). The uncertainty includes the uncertainty in reference flow rate, repeatability and drift.

Table 16 Degree of equivalence (*E* value) for the syringe pump intercomparison.

| flow rate (µl/min) | BHT | CETIAT | DTI | IPQ | METAS | MIKES | VSL |
|--------------------|------|--------|------|------|-------|-------|------|
| 2 | 0.07 | 0.83 | 0.22 | 0.72 | 0.36 | 0.42 | 0.05 |
| 10 | 0.06 | 0.32 | 0.08 | 0.69 | 0.31 | 0.01 | 0.01 |
| 33 | 0.01 | 0.45 | 0.09 | 0.89 | 0.92 | - | 0.74 |
| 100 | 0.08 | 0.27 | 0.03 | 0.08 | 0.47 | - | 0.49 |
| 333 | 0.04 | 0.87 | 0.03 | 0.08 | 0.81 | - | 0.16 |

Table 17 Comparison reference value and uncertainty for the syringe pump.

| flow rate (µl/min) | error | uncertainty |
|--------------------|-------|-------------|
| 2 | -1.76 | 0.47 |
| 10 | -0.03 | 0.28 |
| 33 | 0.24 | 0.18 |
| 100 | -0.03 | 0.14 |
| 333 | -0.14 | 0.16 |

Table 18 Observed chi-squared value χ_{obs}^2 , population size n and threshold $\chi^2(n - 1)$ for the syringe pump intercomparison.

| flow rate (µl/min) | n-1 | χ_{obs}^2 | $\chi^2(n - 1)$ |
|--------------------|-----|----------------|-----------------|
| 2 | 5 | 4.86 | 11.1 |
| 10 | 5 | 2.08 | 11.1 |
| 33 | 4 | 6.80 | 9.5 |
| 100 | 4 | 1.56 | 9.5 |
| 333 | 4 | 3.98 | 9.5 |

6.2 Flow meter

In Figure 4 the calibration results for the flow meter are shown. The plotted flow rates have been given an artificial offset compared to the target flow rate for reasons of visibility. For example, the last series of measurements all have a target flow rate of 200 g/h. Note, the indicated flow rates are not exactly similar for the various labs (see again Table 11). Nevertheless, all flow points are treated as if the indicated flow rate is the same. For the larger flow rates the calibration curve of the meter is quite flat which makes this a fair assumption. For the lowest two flow points the significant calibration uncertainty covers for this mismatch.

The uncertainty in Figure 4 include the uncertainty in reference flow rate, repeatability and the drift (see Section 5.1.2). Next, in Table 19 the E_n value is given, whereas in Table 20 the reference value (equation (4)) and uncertainty (equation (5)) are given. Finally, in Table 21 the final results from the chi-squared test are given (following equation (6) and (8)).

First, the results in Table 19 to Table 21 are found when the results are discarded from CETIAT for the highest flow point. This particular measurement is classified as an outlier following the chi-squared test and therefore does not contribute the RV. Next, from Figure 4 and Table 19, it follows all other results are consistent, there are however two warnings (CETIAT and VSL). Note 1, the highest flow rate is measured with a different balance at VSL, which could cause the large difference in E_n values for the lower flow rates. Note 2, following Figure 4, the mean of the error of the lowest flow point is somewhat higher than the other flow points. This could either be an artifact of the flow meter or caused by one or more outliers in the measured results. However, following the chi-squared test, the measurement data and RV is accepted, hence no outlier has been identified. The zero stability of the meter makes it less suitable for flow rates below, say, 2 g/h.

Table 19 Degree of equivalence (E_n value) for the flow meter intercomparison. Soft colored cells indicate a warning, hard colored cells indicate a fail. Values in red do no contribute to the RV.

| flow rate (g/h) | BHT | CETIAT | DTI | IPQ | METAS | VSL |
|-----------------|------|--------|------|------|-------|------|
| 0.5 | 0.43 | 0.86 | 0.75 | 0.09 | - | 0.57 |
| 2 | 0.51 | 0.68 | 0.60 | 0.70 | 0.15 | 0.34 |
| 6 | 0.48 | 0.47 | 0.30 | 0.68 | 0.40 | 0.29 |
| 20 | 0.30 | 0.74 | 0.14 | 0.61 | 0.31 | 0.26 |
| 60 | 0.57 | 1.07 | 0.45 | 0.21 | 0.53 | 0.06 |
| 200 | 0.61 | 2.63 | 0.92 | 0.29 | - | 1.01 |

Table 20 Comparison reference value and uncertainty for the flow meter.

| flow rate (g/h) | error | uncertainty |
|-----------------|-------|-------------|
| 0.5 | -0.36 | 1.51 |
| 2 | -0.48 | 0.32 |
| 6 | -0.25 | 0.14 |
| 20 | -0.18 | 0.06 |
| 60 | -0.21 | 0.05 |
| 200 | -0.10 | 0.04 |

Table 21 Observed chi-squared value χ^2_{obs} , population size n and threshold $\chi^2(n-1)$ for the flow meter intercomparison. The last flow rate point of CETIAT have not been included.

| flow rate (g/h) | n-1 | χ^2_{obs} | $\chi^2(n-1)$ |
|-----------------|-----|----------------|---------------|
| 0.5 | 3 | 4.33 | 7.81 |
| 2 | 4 | 4.84 | 9.49 |
| 6 | 4 | 3.53 | 9.49 |
| 20 | 4 | 3.97 | 9.49 |
| 60 | 4 | 5.31 | 9.49 |
| 200 | 3 | 5.75 | 7.81 |

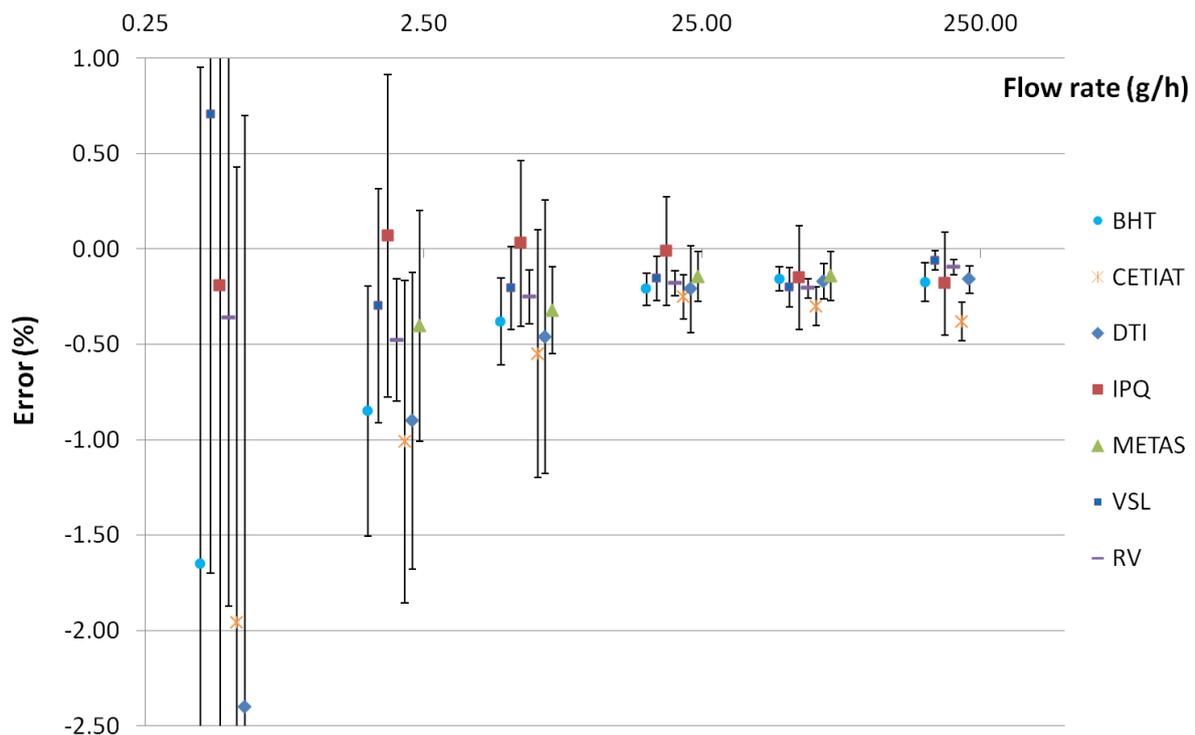


Figure 4 Results intercomparison for the flow meter. The uncertainty includes the uncertainty in reference flow rate, repeatability and the uncertainty due to drift. The indicated flow rate has been modified for visibility. See Table 13 for the calibration uncertainty of the lowest flow point.

6.3 Summary

In Table 22 the E_n values for all flow points (flow meter and syringe pump) are given. The flow rates without parentheses are performed points, flow rates between parentheses give the equivalent of the volumetric or mass flow rate. From this table it follows all results are consistent except for the highest flow point by CETIAT. Further, two are three warnings (CETIAT and VSL). The value for the syringe pump 10 $\mu\text{l}/\text{min}$ has been updated by IPQ after draft A had been released. The original value led to a warning, however was discarded because the average included measurements that likely were influenced by air bubbles (first measurement).

Table 22 E_n values flow meter and syringe pump for all labs who measured both transfer standards. FM stands for flow meter, SP stands for syringe pump. The flow rates without parentheses are performed points, flow rates between parentheses only give the equivalent of the volumetric or mass flow rate.

| Flow rate | | BHT | | CETIAT | | DTI | | IPQ | | METAS | | VSL | |
|-----------|------------------------------|------|------|--------|------|------|------|------|------|-------|------|------|------|
| (g/h) | ($\mu\text{l}/\text{min}$) | FM | SP | FM | SP | FM | SP | FM | SP | FM | SP | FM | SP |
| (0.12) | 2 | | 0.07 | | 0.83 | | 0.20 | | 0.72 | | 0.36 | | 0.05 |
| 0.5 | 8 | 0.43 | | 0.86 | | 0.75 | | 0.09 | | - | | 0.57 | |
| (0.6) | 10 | | 0.06 | | 0.32 | | 0.08 | | 0.69 | | 0.31 | | 0.01 |
| 2 | 33 | 0.51 | 0.01 | 0.68 | 0.45 | 0.60 | 0.09 | 0.70 | 0.89 | 0.15 | 0.92 | 0.34 | 0.74 |
| 6 | 100 | 0.48 | 0.08 | 0.47 | 0.27 | 0.30 | 0.03 | 0.68 | 0.08 | 0.40 | 0.47 | 0.29 | 0.49 |
| 20 | 333 | 0.30 | 0.04 | 0.74 | 0.87 | 0.14 | 0.03 | 0.61 | 0.08 | 0.31 | 0.81 | 0.26 | 0.16 |
| 60 | (1000) | 0.57 | | 1.07 | | 0.45 | | 0.21 | | 0.53 | | 0.06 | |
| 200 | (3333) | 0.61 | | 2.63 | | 0.92 | | 0.29 | | - | | 1.01 | |

7 Conclusion

Eight laboratories participated in EURAMET project 1291/ EURAMET.M.FF.S7; a first intercomparison for low liquid flow rates in Europe. In Table 23 the (preliminary) CMC claims (if existing) are shown for the (mass) flow rates. Most CMC claims are preliminary because they are pending at, or to be submitted to, the BIPM or national accreditation bodies. For all labs it typically holds that the uncertainty increases for a decrease in flow rate.

Next, in Table 24 and Table 25 the best (lowest) calibration uncertainty is shown (based on the syringe pump and flow meter). In the former table the uncertainty due to drift is not included, whereas in the latter table it is. The calibration uncertainty for 0.5 g/h and achieved with the flow meter is discarded because of the large contribution of the zero stability (furthermore an even lower flow point of the syringe pump is available).

Finally, in Table 26 an overview is given of lowest calibration uncertainty (with and without drift) as well as the (preliminary) CMC claims. All results are consistent with the (preliminary) CMC claims except for the highest flow rate measured by CETIAT. In Appendix A possible explanations are given for this inconsistency.

Comparison of primary standards for liquid micro flow rates

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Table 23 (Preliminary) CMC claims (%) ($k=2$) of the participating labs.

| target flow rate (g/h) | target flow rate ($\mu\text{l}/\text{min}$) | BHT | CETIAT | DTI | IPQ | METAS | VSL |
|------------------------|---|------|--------|------|-----|-------|------|
| (0.12) | 2 | N/A | N/A | N/A | 2.5 | 0.7 | N/A |
| 0.5 | 8 | N/A | N/A | N/A | 2.5 | 0.5 | 1.0 |
| (0.6) | 10 | N/A | N/A | N/A | 2.5 | 0.3 | 1.0 |
| 2 | 33 | 0.31 | 0.6 | 2.5 | 0.6 | 0.2 | 0.3 |
| 6 | 100 | 0.12 | 0.6 | 0.6 | 0.4 | 0.15 | 0.3 |
| 20 | 333 | 0.06 | 0.1 | 0.2 | 0.4 | 0.15 | 0.15 |
| 60 | (1000) | 0.05 | 0.1 | 0.07 | 0.3 | 0.15 | 0.10 |
| 200 | (3333) | 0.05 | 0.1 | 0.05 | 0.3 | N/A | 0.05 |

Table 24 Best calibration uncertainty without drift.

| target flow rate (g/h) | target flow rate ($\mu\text{l}/\text{min}$) | BHT | CETIAT | DTI | IPQ | METAS | MIKES | VSL |
|------------------------|---|------|--------|------|------|-------|-------|------|
| (0.12) | 2 | 5.05 | 0.87 | 1.45 | 0.87 | 0.68 | 4.20 | 2.29 |
| (0.6) | 10 | 1.03 | 0.63 | 4.18 | 0.60 | 0.31 | 3.00 | 0.93 |
| 2 | 33 | 0.31 | 0.62 | 0.52 | 0.58 | 0.20 | N/A | 0.21 |
| 6 | 100 | 0.12 | 0.61 | 0.69 | 0.24 | 0.12 | N/A | 0.10 |
| 20 | 333 | 0.06 | 0.10 | 0.22 | 0.28 | 0.12 | N/A | 0.10 |
| 60 | (1000) | 0.06 | 0.10 | 0.09 | 0.27 | 0.13 | N/A | 0.10 |
| 200 | (3333) | 0.10 | 0.10 | 0.07 | 0.27 | N/A | N/A | 0.05 |

Table 25 Best calibration uncertainty including drift.

| target flow rate (g/h) | target flow rate ($\mu\text{l}/\text{min}$) | BHT | CETIAT | DTI | IPQ | METAS | MIKES | VSL |
|------------------------|---|------|--------|------|------|-------|-------|------|
| (0.12) | 2 | 5.06 | 0.94 | 1.49 | 0.95 | 0.77 | 4.22 | 2.32 |
| (0.6) | 10 | 1.05 | 0.66 | 4.18 | 0.64 | 0.37 | 3.01 | 0.95 |
| 2 | 33 | 0.37 | 0.66 | 0.78 | 0.59 | 0.25 | N/A | 0.61 |
| 6 | 100 | 0.17 | 0.61 | 0.72 | 0.25 | 0.23 | N/A | 0.22 |
| 20 | 333 | 0.08 | 0.12 | 0.23 | 0.29 | 0.13 | N/A | 0.12 |
| 60 | (1000) | 0.06 | 0.10 | 0.09 | 0.27 | 0.13 | N/A | 0.10 |
| 200 | (3333) | 0.10 | 0.10 | 0.07 | 0.27 | N/A | N/A | 0.05 |

Comparison of primary standards for liquid micro flow rates

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Table 26 Consistency with (preliminary) CMC claims. Id stands for 'NMI Service Identifier' or an Identifier used for national accreditation.

| NMI/ Inst. | preliminary CMC tables/ national accreditation | | | Comparison EURAMET.M.FF.S7 | | Consistent with (prelim.) CMC tables |
|------------|--|---|------|---|---|--------------------------------------|
| | Flow range (g/h) | Expanded uncertainty (%) | Id | Expanded uncertainty without drift (%) | Expanded uncertainty with drift (%) | |
| BHT | 1-200 | 0.65 (1 -2 g/h) 0.35 (2-10 g/h) 0.1 (10 – 200 g/h) | TBD | 0.31 (2 g/h) 0.12 – 0.31 (2 – 6 g/h) 0.06 – 0.10 (20 – 200 g/h) | 0.37 (2 g/h) 0.17 – 0.37 (2 – 6 g/h) 0.06 - 0.10 (20 – 200 g/h) | yes |
| CETIAT | 1-8000 | 0.6 (1 – 10 g/h) 0.1 (10 – 8000 g/h) | TBD | 0.61 – 0.62 (2 – 6 g/h) 0.10 (20 – 200 g/h) | 0.61 – 0.66 (2 – 6 g/h) 0.1 – 0.12 (20 – 200 g/h) | 88% ^{1,2} |
| DTI | 1-6000 | 4.0 – 0.05 | DK34 | 0.07 – 0.52 (2 – 200 g/h) | 0.07 – 0.78 (2 – 200 g/h) | yes |
| IPQ | 0,12-600 | 2.5 -0.3 | TBD | 0.27 – 0.87 | 0.3 – 2.5 | yes |
| METAS | 0.006 - 60 | 0.70 (0.006 – 0.2 g/h) 0.50 (0.2 – 0.6 g/h) 0.30 (0.6 – 2 g/h) 0.20 (2 – 6 g/h) 0.15 (6 – 60 g/h) | TBD | 0.68 (0.12 g/h) 0.31 (0.6 g/h) 0.20 – 0.31 (0.6 – 2 g/h) 0.12 – 0.20 (2 – 6 g/h) 0.12 – 0.13 (6 – 60 g/h) | 0.77 (0.12 g/h) 0.37 (0.6 g/h) 0.25 – 0.37 (0.6 – 2 g/h) 0.23 – 0.25 (2 – 6 g/h) 0.13 – 0.23 (6 – 60 g/h) | yes |
| MIKES | N/A | N/A | N/A | 3.0 – 4.2 | 3.0 – 4.2 | N/A |
| VSL | 0.25 – 600 | 1.0 – 0.15 (0.25 – 20 g/h) 0.15 – 0.05 (20 – 600 g/h) | TBD | 1.0 – 0.10 (0.6 – 20 g/h) 0.10 – 0.15 (20 – 600 g/h) | 1.0 – 0.3 (0.6 – 20 g/h) 0.12 – 0.05 (20 – 600 g/h) | yes ² |

1) The calibration results for the largest flow rate (200 g/h, flow meter) have been found to be inconsistent ($E_n > 1$).

2) For one flow point a warning has been given.

Appendix A Comments on inconsistency CETIAT highest flow point

Following draft A of this report, an assessment of the possible causes for the observed inconsistency for the highest flow by CETIAT has been performed by CETIAT. This appendix briefly describes the findings of that assessment. A repetition of the same flow points for the transfer standard revealed the same results were obtained, which at least shows good reproducibility.

- Overshoot.** For the highest flow rates, an increase of the flow rate due to the pressurized water (valve closed) in the capillaries systematically occurs. This increase is seen by the flow meter and appears in the recorded data as a peak at the beginning of the measurement. However, the procedures used at CETIAT at the time of the comparison for the "measured flow rate" calculation did not take into account this peak. This approximation led to an under-estimated value for the flow rate of the meter. Consequently, the procedures have been modified to systematically include all data between start and stop of the measurement. The following figures illustrate the problem and its solution.

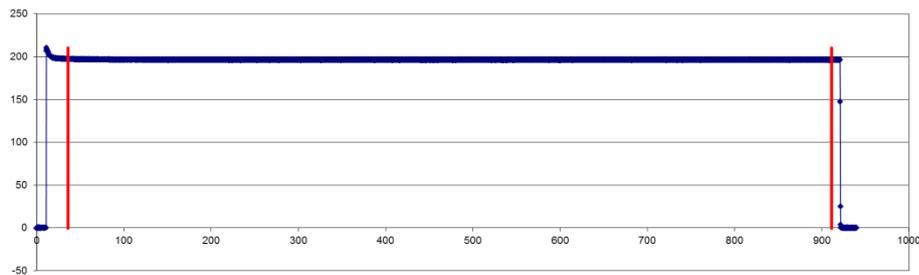


Figure 1 Example of overshoot not taken into account during the comparison at CETIAT. The red lines indicate the start and stop of the calibration.

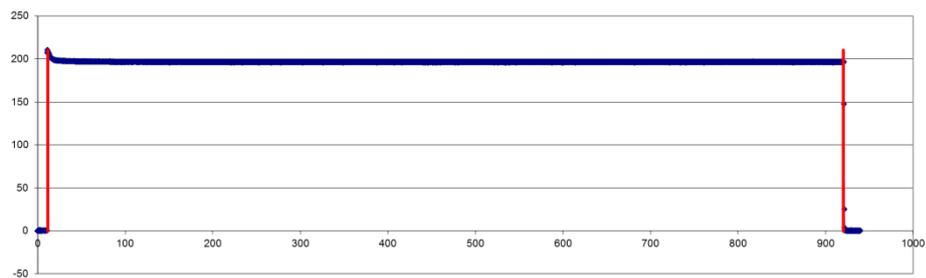


Figure 2 Example of overshoot taken into account in the new procedure implemented at CETIAT after the comparison. The red lines indicate the start and stop of the calibration.

- Timing error.** The synchronization of mass and time data is critical in the gravimetric start/stop method. This is done by time-stamping the mass information sent by the balance. Although it is taken into account in the uncertainty budget, a systematic timing error can occur due to different time delays in the acquisition system. To reduce this potential error cause, a real time

dynamic ("flying" method) acquisition system linked to a reference atomic clock is being developed at CETIAT. This will also reduce the potential error due to variation of flow rate at the beginning of the measurements, and strengthen the uncertainty on time measurement.

- **Variation of surface tension effect.** Although this parameter has been theoretically calculated with the dimensions of the weighing ensemble (capillary, capillary end, reservoir), it has not been measured yet. A dedicated test rig for investigating and quantifying surface tension effect on the weighing systems of CETIAT's micro-flow calibration bench is under development. This will strengthen the uncertainty budget on mass measurement.
- **Bubbles in the circuit.** The last possible cause for a reference flow rate measurement deviation is the presence of bubbles in the circuit downstream to the flow meter. This is especially critical for the capillaries used at 60 g/h and 200 g/h that have additional connectors (and therefore dead volumes). The following picture shows the capillaries used for 60 g/h and 200 g/h (red arrows). An ongoing project at CETIAT is intended to reduce the number of capillaries and connectors in order to reduce the risk of air bubbles entrapped in the system.

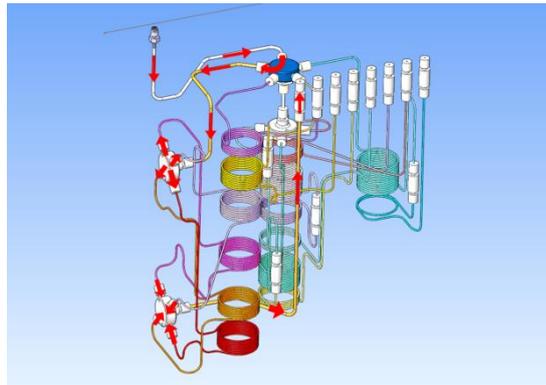


Figure 3 Capillaries system of CETIAT's micro-flow facility with circuit used by water for 60 g/h and 200 g/h shown as red arrows.

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